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**LITERATURE SURVEY ON SYNTHESIS, PROPERTIES,  
AND  
APPLICATIONS OF SELECTED BORIDE COMPOUNDS**

*Barry R. Emrich*

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December 1962

Directorate of Materials and Processes  
Aeronautical Systems Division  
Air Force Systems Command  
Wright-Patterson Air Force Base, Ohio

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Rpt No. ASD-TDR-62-873. LITERATURE SURVEY ON SYNTHESIS, PROPERTIES, AND APPLICATIONS OF SELECTED BORIDE COMPOUNDS. Final report, Dec 62, 122p., incl illus., tables, 165 refs.

Unclassified Report

A comprehensive review of the literature was made to assist in providing background information needed for future work concerning boride materials. The materials reviewed included solid bodies of TiB<sub>2</sub>, ZrB<sub>2</sub>, HfB<sub>2</sub>, VB<sub>2</sub>,

( over )

NbB<sub>2</sub>, TaB<sub>2</sub>, CrB<sub>2</sub>, and ThB<sub>4</sub>. This compilation presents information on synthesis, properties, and applications of the selected boride compounds, including selected abstracts and articles.

This documentary search, by showing many gaps and wide scatter where information is available, demonstrates the need for the development of authoritative scientific information on borides applicable to future technological requirements.

1. Boride literature review
2. Boride synthesis properties
3. Boride applications
1. AFSC Project 7382, Task 738103
- II. Emrich, Barry R.
- III. Aval fr OTS
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## FOREWORD

This report is a compilation of information obtained from open literature. The report was prepared by Barry R. Emrich, Ceramics and Graphite Technical Evaluation Section, Materials Information Branch, Applications Laboratory, Directorate of Materials and Processes, Aeronautical Systems Division. This work was done under Project 7381, "Materials Application", Task 738105, "Ceramics and Graphite Technical Evaluation".

This report covers work conducted from 1 February 1962 to 1 August 1962. It has been prepared and is presented as a part of Materials Central's information activities on ceramics and graphite. Other reports reviewing the technology of these materials will be issued in the future.

The author wishes to acknowledge the vital support of the following Aeronautical Systems Division personnel; Captain Yuhas, Directorate of Foreign Technology Analysis, for providing translations from the Russian literature. Mr. C. E. Butler and J. Krochmal, Directorate of Materials and Processes, for interest in the work and supervisory assistance, and Miss Junie Banks, Directorate of Materials and Processes, for providing reprints and the typing necessary in compiling the information.

## ABSTRACT

A comprehensive review of the literature was made to assist in providing background information needed for future work concerning boride materials. The materials reviewed included solid bodies of  $TiB_2$ ,  $ZrB_2$ ,  $HfB_2$ ,  $VB_2$ ,  $NbB_2$ ,  $TaB_2$ ,  $CrB_2$  and  $ThB_4$ . This compilation presents information on synthesis, properties, and applications of the selected boride compounds, including selected abstracts and articles.

This documentary search, by showing many gaps and wide scatter where information is available, demonstrates the need for the development of authoritative scientific information on borides applicable to future technological requirements.

## PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER



D. A. SHINN  
Chief, Materials Information Branch  
Applications Laboratory  
Directorate of Materials & Processes

## TABLE OF CONTENTS

		Page
I.	INTRODUCTION.....	1
II.	BACKGROUND.....	2
III.	SYNTHESIS.....	3
	Synthesis by Fusion.....	4
	Sintering the Powdered Elements, Oxides, Boron or the Metal Hydride below Fusion Temperature.....	5
	Reduction of the Mixture of Metal Oxide and Boron Oxide with Al, Si, Mg, or C.....	9
	Reaction of the Metal, Metal Oxide, or Metal Hydride with Boron Carbide.....	10
	Fused-Salt Electrolysis.....	10
	Chemical Vapor Deposition.....	11
	Single Crystals.....	13
	Procurement of High Purity Diborides.....	14
IV.	PROPERTIES.....	19
	Thermal Properties.....	20
	Crystal Structure.....	32
	Mechanical Properties.....	32
	Chemical Properties.....	40
	Thermo-Physical Properties.....	55
	Electrical Properties.....	62
	Nuclear Properties.....	64
V.	APPLICATIONS.....	66
	REFERENCES.....	69
	APPENDIX I.    SELECTED ABSTRACTS.....	79
	APPENDIX II.   SELECTED ARTICLES.....	87



# LIST OF FIGURES

	Page
1. ARC FURNACE.....	6
2. SCHEMATIC OF METALLOGRAPHIC PROCEDURE FOR $TiB_2$ .....	15
3. COMPARISON OF BORIDE MELTING POINTS WITH OTHER REFRACTORY MATERIALS.....	22
4. THERMAL EXPANSION OF TANTALUM DIBORIDE.....	23
5. THERMAL EXPANSION OF ZIRCONIUM DIBORIDE.....	24
6. THERMAL EXPANSION OF $TiB_2 - ZrB_2 - HfB_2$ .....	25
7. THERMAL EXPANSION OF $CrB_2 - NbB_2 - VB_2 - TaB_2$ .....	26
8. THERMAL CONDUCTIVITY OF ZIRCONIUM DIBORIDE.....	29
9. THERMAL CONDUCTIVITY OF TANTALUM DIBORIDE.....	30
10. DIBORIDE STRUCTURE ( $MB_2$ ).....	33
11. ZIRCONIUM-BORON PHASE DIAGRAM.....	40
12. TITANIUM-BORON PHASE DIAGRAM.....	40
13. CHROMIUM-BORON PHASE DIAGRAM.....	41
14. HAFNIUM-BORON PHASE DIAGRAM.....	41
15. VANADIUM-BORON PHASE DIAGRAM.....	42
16. NIOBIUM-BORON PHASE DIAGRAM.....	42
17. TANTALUM-BORON PHASE DIAGRAM.....	43
18. ENTHALPY AND HEAT CONTENT FOR ZIRCONIUM DIBORIDE.....	58
19. SPECIFIC HEAT OF $TiB_2$ .....	59
20. SPECTRAL EMISSIVITY OF $NbB_2$ FROM 0.4-5.0 MICRONS AND AT 1540°K, 1800°K, 2000°K.....	61

# LIST OF TABLES

	Page
I. REFERENCES ON SYNTHESIS OF SPECIFIC DIBORIDES.....	4
II. SINTERING SCHEDULES FOR CERTAIN DIBORIDES.....	7
III. EFFECT OF HOLDING TIME UNDER PRESSURE OF 120 Kg/cm <sup>2</sup> AT SINTERING TEMPERATURE OF 2300°C FOR TITANIUM DIBORIDE...	8
IV. DENSITY OF SPECIMENS PRODUCED BY HOT PRESSING WITH EXTERNAL LOAD REMOVED ON COOLING.....	8
V. HOT PRESSING OF PRODUCTS FROM CERTAIN DIBORIDES.....	9
VI. FUSION ELECTROLYSIS OF ZIRCONIUM AND TITANIUM DIBORIDES...	11
VII. PROCUREMENT SOURCES FOR TiB <sub>2</sub> .....	17
VIII. PROCUREMENT SOURCES FOR ZrB <sub>2</sub> .....	17
IX. PROCUREMENT SOURCES FOR NbB <sub>2</sub> .....	18
X. PROCUREMENT SOURCES FOR TaB <sub>2</sub> .....	18
XI. PROCUREMENT SOURCES FOR HfB <sub>2</sub> .....	19
XII. MELTING POINTS.....	20
XIII. TABULATION OF MELTING POINTS OF DIBORIDES.....	21
XIV. THERMAL EXPANSION.....	21
XV. THERMAL EXPANSION OF BORIDES.....	27
XVI. THERMAL CONDUCTIVITIES.....	31
XVII. HEAT CAPACITY.....	31
XVIII. CRYSTAL STRUCTURES AND LATTICE PARAMETERS.....	32
XIX. DENSITY.....	32
XX. HARDNESS.....	34
XXI. MICROHARDNESS AS A FUNCTION OF LOAD.....	35
XXII. BENDING STRENGTH.....	35
XXIII. BENDING STRENGTH TiB <sub>2</sub> .....	36
XXIV. BENDING STRENGTH VB <sub>2</sub> .....	36
XXV. HOT DEFORMATION TEST OF TiB <sub>2</sub> .....	37
XXVI. COMPRESSIVE STRENGTH.....	37
XXVII. ELASTIC MODULUS.....	38
XXVIII. ELASTIC CONSTANTS OF TiB <sub>2</sub> .....	38
XXIX. DESIGN CHARACTERISTICS.....	39
XXX. DIFFUSION IN TANTALUM-BORON SYSTEM.....	44
XXXI. DIFFUSION IN NIOBIUM-BORON SYSTEM.....	45
XXXII. DIFFUSION IN TITANIUM-BORON SYSTEM.....	45
XXXIII. CHEMICAL COMPOSITION CHANGE IN VACUUM AFTER HEATING TO 1700°C.....	45
XXXIV. CORROSION DEPTH IN OXIDATION OF CERTAIN DIBORIDES.....	46
XXXV. CHEMICAL-CORROSION RESISTANCE.....	47
XXXVI. REFRACTORY PROPERTIES.....	49
XXXVII. STABILITY IN ACIDS.....	52
XXXVIII. SOLUBILITY IN NaOH SOLUTIONS.....	52
XXXIX. SOLUBILITY IN ACIDS.....	53
XXXX. SOLUBILITY OF MIXED ACIDS.....	54
XXXXI. EVAPORATION BEHAVIOR AND VAPOR PRESSURE.....	55
XXXXII. EVAPORATION-VAPOR-PRESSURE IN A VACUUM.....	55
XXXXIII. HEATS OF FORMATION.....	56

# LIST OF TABLES (CONTINUED)

	Page
XXXXIV. ENTROPY.....	57
XXXXV. THERMIONIC EMISSION.....	57
XXXXVI. SPECIFIC HEAT OF $TiB_2$ .....	57
XXXXVII. STOICHIOMETRIC CHARACTERISTICS AND SPECIFIC GRAVITY.....	60
XXXXVIII. ELECTRICAL RESISTIVITIES.....	62
XXXXIX. HALL COEFFICIENT - THERMO-EMF.....	63
XXXXX. SUPERCONDUCTIVITY.....	63
XXXXXI. WIEDEMANN-FRANZ RATIOS.....	63
XXXXXII. RADIATION.....	64
XXXXXIII. COMPATIBILITY OF BORIDE WITH TITANIUM MATRIX.....	64
XXXXXIV. COMPATIBILITY OF BORIDE WITH ZIRCONIUM MATRIX.....	65
XXXXXV. COMPATIBILITY OF BORIDE WITH 304 STAINLESS STEEL MATRIX.....	65
XXXXXVI. COMPATIBILITY OF BORIDE WITH IRON MATRIX.....	65
XXXXXVII. COMPATIBILITY OF BORIDE WITH NICKEL BASE.....	65
XXXXXVIII. COMPATIBILITY OF $UO_2$ WITH BORIDES.....	66

## I. INTRODUCTION

According to a recent Materials Advisory Board Committee report, (1) borides exhibit desirable properties useful in many high temperature structural applications where other materials would fail. Research data indicates that above 2000°C (3632°F) certain borides can be produced with relatively good strength and oxidation resistance. Borides can be used at temperatures and environments where graphite and refractory metals will oxidize and where oxides are weak. The refractory borides have high electrical conductivity, intermediate thermal expansion and thermal conductivity.

Borides have properties intermediate between the carbides and oxides. Their melting points are significantly below the carbides, but oxidation resistance is stated to be greater. In contrast to the oxides, the borides retain their strength at high temperatures. Good chemical stability of the borides indicates they can be used in contact with other materials such as graphite, carbides, metal, and oxides with minimum reaction. To evaluate the full potential of the borides, the state of development of these materials must be greatly advanced. Before initiating a program on the development of borides, knowledge of past investigation is essential. This report was prepared to assist in providing the background for such a program.

Since there are many boride compounds known to exist, it was necessary to be somewhat arbitrary in selecting specific borides of primary interest. This report covers a literature search on solid bodies of selected binary boride compounds. The binary compounds were chosen on the bases of gaining the most fundamental knowledge of borides in general. The diborides of titanium, zirconium, hafnium, vanadium, niobium, tantalum, and chromium, as well as thorium tetraboride were selected because of their potential use in high temperature structural applications, and the fact that they are the highest melting compounds known to exist in each of their respective equilibrium phase systems.

This report includes sections on synthesis, properties, and applications, references, selected abstracts and articles. The synthesis section summarizes and briefly discusses the general methods used in obtaining boride raw materials through chemical reactions. The discussion is presented with comments viewed toward synthesis of high purity diboride compounds.

The property section is a compilation of a range of properties with comparisons of properties obtained by various investigators. The majority of this section consists of tables with selected abstracts and articles provided in the Appendices. Only selected abstracts or articles published since 1954 are included. An article was included if it was the latest and most reliable information on the subject and loss of detail would limit the value of the data. Some of the data listed in the tables may be of questionable value because measurements were made on specimens of incomplete specifications as

to purity, porosity, and thermal treatment. Nevertheless, this compilation may be of value to materials engineers and research scientists since it indicates work performed and references have been included for retrieval of original publications.

The applications section covers potential high temperature technological uses, with a brief discussion on industrial applications of the selected boride compounds.

It is intended that this survey serve as a reference for materials engineers in obtaining information to serve as a basis for prediction of test results and decisions for future investigations. This compilation also summarizes the methods for producing high purity borides and should acquaint the designer with potential high temperature applications.

\*As additional information, several sources of supply for high purity diborides are tabulated, with cost and degree of purity provided. These sources are for general information only, and are not intended to represent a complete or necessarily precise indication of either number of sources or cost of these materials. They are provided simply to make this report as complete as practical at the time of writing.

## II. BACKGROUND

The pioneering work on borides began around 1895 with the work of Moissan (2), Tucker and Moody (3) performed some early work on zirconium borides in 1901. From the turn of the century to about 1945 very little attention was paid to the borides. However, during this interval some investigations were performed, the principal investigators of which included Wedekind (4), Krupp (5), Moers (6,7), Andrieux (8), Meissner (9), Becker (10), and Anderson (11). An article concerning a large scale manufacturing process of  $ZrB_2$  was published by McKenna (12) in 1936.

Since 1945 renewed interest has grown and more intensive research has been performed. Much of the first work was in determining the large number of borides which are now known to exist. An investigation of the chemical and physical properties was started under a Navy contract (13). In 1949 Kiessling (14) and also work by Norton, Blumenthal and Sindeband (15) determined structure of zirconium diboride. A number of diborides were investigated by Brewer and co-workers (16) in 1951. Experiments on pressure sintering of the diborides were reported by Glaser (17) in 1951. Between 1952 and 1953 Glaser and Post (18-21) published four papers which included work on zirconium borides.

Schwarzkopf and Kieffer (22) reported a review of the processes involved in the preparation of borides. Another review by Campbell (23) clearly showed that the borides of groups IV, V, and VI had received most study up to 1956. During this same interval Samsonov (24) was performing some basic studies on the borides.

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\*Selected data compiled from First Monthly Report under Contract AF 33(657)-8635, 25 April 1962.

Epelbaum and Gurevich (25) in 1958, determined accurately the lattice parameters of  $ZrB_2$ . A brief description of binary and ternary boride systems formed between high-melting metals and boron was presented in a book by Samsonov and Portnoy (26) in 1960. A description of the fabrication methods for borides was recently reported by Hausner (27). Another major investigation at this time was on the thermodynamic properties of refractory borides by Leitnaker (28).

Due to the lack of reliable information obtainable from the earlier investigations and the recent technological requirements for improved materials the Materials Advisory Board (1) recommended a plan for yearly expenditures on boride studies. The result of their recommendation is now being realized in Air Force Contract 33(657)-8635 which was initiated in May 1962.

### III. SYNTHESIS

The primary interest of this section is to summarize the reactions which occur in obtaining diboride raw materials used for further processing. Those reactions or methods which would be most suitable for providing high purity diborides were of special concern. Since this discussion on synthesis has a high purity theme, a section on single crystals and procurement of high purity diborides was included.

The six basic principle reactions involving synthesis of diborides or borides in general are listed below (22,29):

1. Fusing the direct combination of metal with boron ( $Me \neq B_2 = MeB_2$ ).
2. Reduction of mixtures of metal oxides and boron anhydride with carbon ( $MeO \neq B_2O_3 \neq C \rightarrow MeB_2 \neq CO$ ). Sintering the powdered elements, metal hydride and boron or the oxides, below fusion temperature.
3. A thermite reaction reducing a mixture of metal oxides and excess  $B_2O_3$  with aluminum, magnesium, or silicon. ( $MeO \neq B_2O_3 \neq Al(Mg, Si) \rightarrow MeB_2 \neq Al(Mg, Si)_xO_4$ ).
4. Reaction of the metal oxide, metal or metal hydrides with boron carbide, with or without the addition of  $B_2O_3$  ( $Me(MeO, MeH, MeC) \neq B_4C \neq B_2O_3 \neq MeB_2 \neq CO$ ), or  $MeO \neq B_4C \neq C \rightarrow MeB_2 \neq CO$ ).
5. Electrolysis of fused-salt baths containing the metal oxide, various halide fluxes, and boron oxide (alkali oxide  $\neq$  alkali halide  $\neq B_2O_3 \neq MeO \neq MeB_2$ ; example:  $2CaO \neq CaF_2 \neq 2B_2O_3 \neq \frac{1}{2} TiO_2 \rightarrow TiB_2$  (23)).
6. Vapor phase deposition (example:  $HfCl_4 \neq B_2Br_3 \neq H_2 \rightarrow HfB_2 \neq HCl \neq HBr$ ). Several methods are used in vapor deposition reactions.

Table I provides a quick summary to the investigations performed concerning the six basic reactions and the diborides of interest for this specific report. Most of the work to date has been performed on titanium and zirconium diborides, with relatively little work having been done on the other diborides.

In general the literature points out that reactions 3, 4, and 5, which have received the majority of previous study, would be of greatest interest for low cost commercial production and do not show promise for preparation of controlled materials. Reactions 1, 2, and 6 would most likely be used for the synthesis of high purity research specimens. The direct combination of boron and the relevant metal is the most usual method used for the synthesis of pure diborides. Sintering, hot pressing and vapor deposition techniques yield aggregates ready for final shaping, which may make them more suitable for use than the fusion method. Recent study in the area of single crystal growth by Linde Company (30, abstract in Appendix 2) will no doubt improve the capability of making ultra pure testing materials. Abstracts 2 - 10 of Appendix I are concerned with the methods of synthesis as discussed in the following paragraphs.

TABLE I: REFERENCES ON SYNTHESIS OF SPECIFIC DIBORIDES

Material	References Listed by Synthesis Methods						
	1	2	3	4	5	*6	**7
TiB <sub>2</sub>	30,31	16,46,47,52	12,15,59	36,37,48	8,15,38,49, 56,60,61	6,18	39
ZrB <sub>2</sub>	14	18,50,51,52	12,15,59	37,53,54,55	15,38,60,61	6	39,57
HfB <sub>2</sub>	18	52				6,62	
VB <sub>2</sub>		12,52	59	18,37	8,38	6	
NbB <sub>2</sub>		16,18,52		18,37	8,15		39
TaB <sub>2</sub>		14,16,52	12	18,37	8,15,38		39
CrB <sub>2</sub>	14	52	59		38,58		
ThB <sub>4</sub>		16,18					

\*Does not include references concerning coatings.

\*\*General discussions on synthesis methods.

1. Synthesis by Fusion: Synthesis of high melting diboride compounds by solidification from the melt involves melting the metal directly with boron or heating presintered mixtures of the two materials. This method allows a high degree of control and generally produces a uniformly reacted pure compound. The final product could be used as a source of diborides for subsequent sintering or hot pressing, as for example in some powder metallurgical production methods.

Early experiments did not provide pure borides. It was not until about 1949 that pure diborides were produced using this method. Recent investigations by Kieffer (30), Westbrook (31) show how the direct fusion process and pre-sintering followed by melting can be used for obtaining materials suitable for crystal growth.

Since the melting temperatures of the subject materials range between chromium diboride ( $\cong 2280^{\circ}\text{C}$ ,  $4135^{\circ}\text{F}$ ) and hafnium diboride ( $\cong 3250^{\circ}\text{C}$ ,  $5880^{\circ}\text{F}$ ) electric arc, arc image, electron beam or focused induction heating is suitable for melting purposes. A graphite container is generally used to eliminate impurities during melting. An example of a laboratory arc furnace which eliminated impurities from occurring between the liquid and crucible material or reactive gas is shown in Figure 1. This specific furnace was used by Stanford Research Institute (32, see abstract in Appendix II) during a recent investigation on synthesis of high temperature materials.

Another technique proposed recently by Stanford Research for synthesis of high melting compounds which would require high pressure to prevent thermal decomposition is termed implosive shock. This method was demonstrated by the Stanford Research Institute (32) in the synthesis of boron phosphide. These experiments consisted of placing mixtures of the two components into a mild steel cylinder which was encased in a layer of explosive. The explosive was detonated at one end, causing a peripheral detonation to sweep along the surface of the cylinder with a velocity of about 7900 meters per second. A cylindrical converging shock wave induced in the steel, produced a pressure at the center of about  $2 \times 10^6$  atmospheres for approximately  $5 \times 10^{-6}$  seconds. During this short time the temperature of the specimen reached several thousand degrees Kelvin. Difficulties of this method were contamination of specimen with iron and control of process.

2. Sintering the Powdered Elements, Oxides, Boron or the Metal Hydride (in the Presence of Carbon) below Fusion Temperature: Like the first method this process is adaptable to the production of pure diborides. This solid state reaction method can be used to discover compounds which would be unstable at the highest temperatures and which would form only slowly at lower temperatures.

The metal powders of titanium, zirconium, and hafnium are difficult to prepare in a state of high purity, because these materials are highly reactive with oxygen. For these materials the use of oxide instead of the metal is preferred during synthesis. Another reason for the use of the oxide in place of the metal is their relatively low cost. This low initial cost is counteracted by the fact that oxides cause a reduction in reaction rates due to their bulky state which exist so that undesired reaction products can go off easily. The hydrides ( $\text{MeH}_2$ ) are sometimes used for producing small quantities. They are more expensive than oxides, but not much more expensive than the metals. Boric oxide with its low melting point prevents the use of high reaction temperature therefore reducing reaction rate. If very pure diborides are desired, boron can be used by itself as a reducing agent. The reaction then proceeds



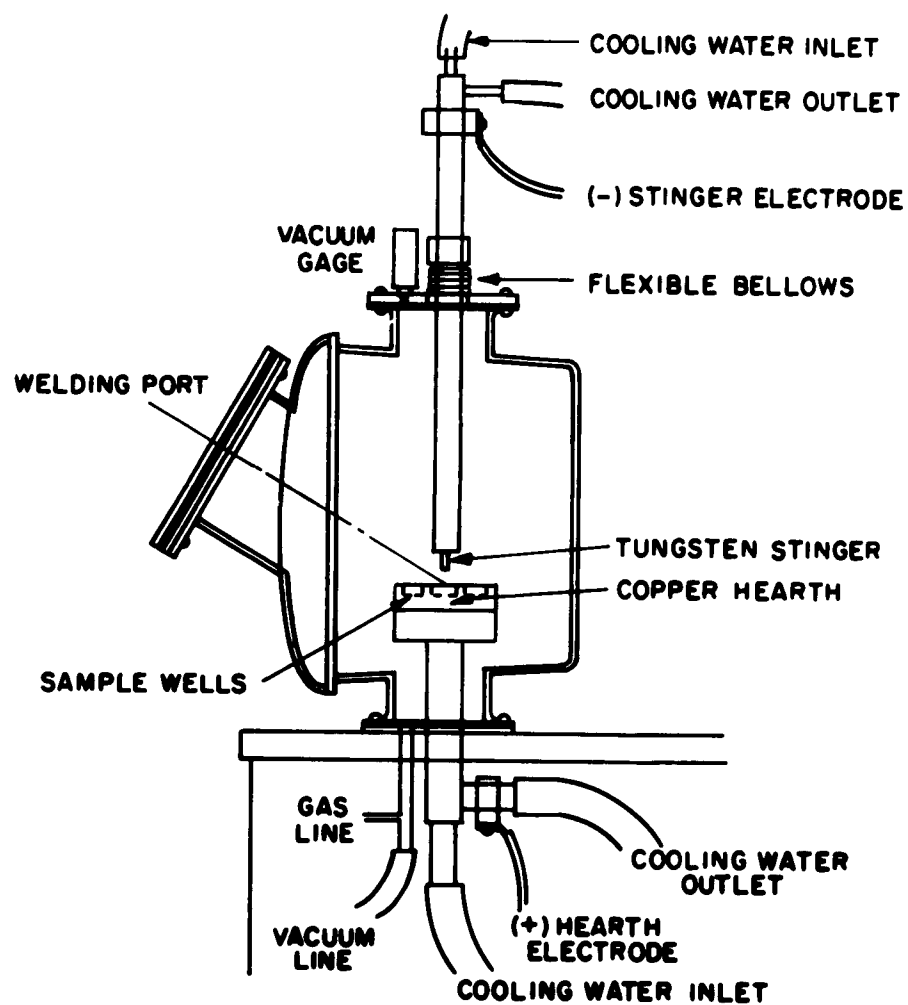


Figure 1. Arc furnace (ref 32)

as follows:  $3\text{MeO}_2 + 10\text{B} \rightarrow 3\text{MeB}_2 + 2\text{B}_2\text{O}_3$ . This method eliminates the  $\text{B}_2\text{O}_3$  in the reaction, which may allow higher reaction temperatures, permitting a more rapid diffusion process. Carbon is the most common reduction material. Carbon leaves no oxide residue, and it will reduce all metal oxides at elevated temperatures. Boron must be added in definite amounts to form the desired diboride (27).

The kinetics of sintering is a compromise between reaction temperature, grain growth and liquid formation. Since large grains reduce driving force for reactions, smaller grains are desirable, however higher reaction temperatures promote diffusion. The formation of a liquid is also undesirable, because it causes the material to lump which greatly reduces the diffusion process. A temperature of approximately  $375^\circ\text{C}$  below the melting point, is generally used during this type of sintering process (27). Sintering has been used extensively to prepare pure diborides by heating the mixed pulverized elements or a metal hydride and boron in a vacuum, low pressure argon, or the hydrogen emitted from the hydride (16). A simple sintering method used by S. V. Samsonov and K. I. Portnoy (26) consisted of firing the boride specimens in a resistance or induction type furnace, with graphite holders. The holder is lubricated with lamellar graphite in glycerine suspension to eliminate adhesion between the sintered article and the holder. The furnace is heated to  $600\text{--}700^\circ\text{C}$ , specimens are then injected into the furnace. The furnace is brought up to sintering point in one to three hours, held at the sintering temperature for 15-30 minutes, and then cooled to  $800$  to  $900^\circ\text{C}$ . Thermal history for sintering of these borides are presented in Table II.

TABLE II: SINTERING SCHEDULES FOR CERTAIN DIBORIDES (26)

Compound	Sintering Temp ( $^\circ\text{C}$ )	Holding Time at Sintering Temp Mins.	Residual Porosity %
$\text{TiB}_2$	2200-2250	15	5-8
$\text{ZrB}_2$	2300	15	3-6
$\text{CrB}_2$	2250	15	6

The sintering times and temperatures in general will vary depending upon specific diboride composition. R. Kiessling (14) prepared chromium borides by sintering the mixed powders in evacuated silica tubes for 48-72 hours at  $1150^\circ\text{C}$ . Tantalum borides were vacuum-sintered for  $\frac{1}{2}$  hour at  $1800\text{--}1900^\circ\text{C}$  or for 100-150 hours at  $1150^\circ\text{C}$  in evacuated silica tubes. The data obtained by Samsonov and Portnoy for the case of  $\text{ZrB}_2$  by the use of  $130 \text{ Kg/cm}^2$  of pressure during the sintering process or a  $60 \text{ Kg/cm}^2$  pressure for a certain period of time followed by a pressure increase to  $130 \text{ Kg/cm}^2$  gave practically identical final densities and shrinkages. After 20 minutes of sintering time the linear shrinkage was approximately 28 percent. (26).

Since pure diborides undergo very little sintering except at very high temperatures (where thermal decomposition may become serious), hot pressing is generally used to produce massive bodies commercially.

Hot pressing forms a dense diboride body. However, contamination of the diboride may occur due to carbon or other impurities from the graphite dies.

Glaser (17) showed that the borides of zirconium and titanium are stable in the presence of carbon at temperatures up to their melting points. Jackson and Palmer (33) produced a liquid phase during pressing of these two diborides at temperatures around 2300°C. If hot pressing is used it should be carried out in a vacuum to limit contamination around the surfaces of the dies. Impurities in this system may also come from the diffusion of impurities in the graphite into the diboride specimen.

To provide a quantitative illustration of what to expect from diboride powders during the sintering and hot-press forming operation, Tables III, IV, and V were compiled from Samsonov's work.

TABLE III: EFFECT OF HOLDING TIME UNDER PRESSURE OF 120 Kg/cm<sup>2</sup> AT SINTERING TEMPERATURE OF 2300°C FOR TITANIUM DIBORIDE (26)

Compound	Holding Time in Sintering (min)		Total	Density g/cm <sup>3</sup>	Residual Porosity (%)
	With Load	Without Load			
TiB <sub>2</sub>	0	5	5	3.78	16.4
	3	2	5	3.89	13.9
	4	1	5	3.96	12.4
	4.5	0.5	5	4.16	8.0
	5.	0.	5	4.20	7.3

\*Theoretical density (g/cm<sup>3</sup>) equals 4.5 for TiB<sub>2</sub>.

TABLE IV: DENSITY OF SPECIMENS PRODUCED BY HOT PRESSING WITH EXTERNAL LOAD REMOVED ON COOLING (SINTERING TEMPERATURE 2350°C, SINTERING TIME 5 MINUTES, PRESSURE 120 Kg/cm<sup>2</sup>) (26)

Compound	Temp. at Which Load was Removed During Cooling °C	Density g/cm <sup>3</sup>	Residual Porosity
TiB <sub>2</sub>	2100	3.16	30.0
	1750	3.25	28.5
	1530	3.57	21.0
	1300	3.95	11.7
	1050	4.17	7.8
	20	4.20	7.3

The density decreases when the load is removed at 1300°C; a progressive decrease in density occurs as the load-relief temperature is increased.

TABLE V: HOT PRESSING OF PRODUCTS FROM CERTAIN DIBORIDES (26)

Compound	Sintering Temp (°C)	Sintering Pressure (Kg/cm <sup>2</sup> )	Sintering Time Minutes	Residual Porosity %
TiB <sub>2</sub>	2330	120	5	0.6-1.0
ZrB <sub>2</sub>	2350	120	10	0
NbB <sub>2</sub>	2580	120	10	0
TaB <sub>2</sub>	2350	120	10	8-9

A recent translation by Marsol (34) concerning the pressing and sintering of diboride powders is included in Appendix II for specific information on this subject. The original work reported was performed by Babich, Portnoy and Samsonov (35).

Jackson and Palmer's (33) hot pressing for TiB<sub>2</sub> and ZrB<sub>2</sub> showed the final densities to be 89.7 and 93.8 g/cc, respectively. Samsonov, et al., (26) as shown in Table IV produces TiB<sub>2</sub> having only 0.6 to 1 percent residual porosity in the sintered product. The variation in results may have been caused by difference in impurities, since the purity of the products were not reported.

Other hot forming methods which might have application for producing dense uncemented diborides are hot isostatic pressing and extrusion. The isostatic process, developed at Battelle and also used by General Electric Company at Cincinnati, makes use of a hot gas as the pressurizing fluid. The advantages of this method are: (1) faster densification than at room temperature; (2) tends to form desirable oriented fabric; (3) capable of producing parts not feasible by hot pressing. The major disadvantage of this system at the present time is the temperature limitation (1650°C, 3000°F).

Hot extrusion does not appear to be a likely prospect because of its dependence on transforming the brittle diborides to a moderately plastic condition. This transition is slow and occurs at relatively high temperatures (1265°C, 2310°F).

3. Reduction of the Mixture of Metal Oxide and Boron Oxide with Al, Si, Mg, or C: This thermite reaction, sometimes referred to as carbothermic, aluminothermic, silicothermic, etc., reduction is based on the metal oxide and B<sub>2</sub>O<sub>3</sub> being reduced by one of the metals and the intermediate products plus the liberated boron reacting to form diborides. This method has two basic faults: (1) The metal oxide formed with the reducing metal must be separated from the boride product or else an impure product will be obtained. (2) Also, due to oxide formation, the composition of the resulting boride is difficult to control. Because of its basic contamination difficulty, only commercial grades of diborides would be produced. This method, like method number 2, uses the cheapest raw materials for the production of diborides, that is the oxides of the metal and boron. This method is basically the same as method number 2, except reduction is accomplished by means of a metal, rather than by carbon. Therefore, similar process temperatures would apply for both methods.

4. Reaction of the Metal, Metal Oxide, or Metal Hydride with Boron Carbide: This method is similar to methods two and three, but boron carbide ( $B_4C$ ) is used as the reduction material. The boron carbide is a high density crystalline material and is commercially available, which is why it is often used today. This process is reacting the powders of the metals or their oxides with boron carbide at approximately  $2000^\circ C$  ( $3630^\circ F$ ) in a graphite container. The major disadvantage of this method is the carbide contamination. The contamination is reduced by the presence of excess  $B_2O_3$ ; however the excess  $B_2O_3$  limits the controlling of the boron content of the product. For these reasons this method, like previous method, would not be satisfactory for use in making highly pure, controlled diborides.

Another means of obtaining borides using this same concept is by hot pressing mixtures of boron carbide with the refractory metals or their hydrides (36). As mentioned in Method 2 the hydrides, which are used as the metal-containing reagent, forms less oxidizable diborides than the metals and are not much more expensive. Since the hydrides are considerably more expensive and difficult to obtain in some cases than the metal oxides, they are generally used for making only small quantities. The hydrides of titanium and zirconium decompose about  $600^\circ C$  ( $1114^\circ F$ ) and  $900-1100^\circ C$  ( $1662-2022^\circ F$ ), producing the metal powders. The hydrogen, given off by the hydrides, provides a highly desirable atmosphere for preparation of pure diborides, but because they are so volatile the reaction is forced to occur at atmospheric pressure and high temperatures  $1900-2000^\circ C$  ( $3463-3642^\circ F$ ) (26).

G. A. Meerson and G. V. Samsonov (37, Article 2 in Appendix II) investigated a vacuum process using the following reaction:  $2MeO + B_4C + C \rightarrow 2MeB_2 + 2CO$ . The lower temperature limit for starting to obtain  $TiB_2$  by this vacuum reaction is  $1100-1150^\circ C$  or approximately  $800^\circ C$  lower than previous mentioned graphite tube hydride reaction. Their work was based on removing carbon as CO from boron carbide using the oxygen of the oxide, additional carbon in the form of carbon black, and combining the boron with the high-melting metal to form the corresponding boride. Since the process involves reducing chemically stable oxides with the formation of a gas (CO), the study of the conditions for performing the process under vacuum was made. The purpose of the vacuum was to reduce nitration or oxidation of the products, and act as a catalyst for the entire reaction. This method is used as an example, but it illustrates the general type of equipment and temperature areas involved with methods two and three using vacuum technology. Methods two, three, and four are basically a reduction process, differing primarily in the materials used for reducing the metal, metal oxide or metal hydride.

In summary the so-called boro carbide method of producing diborides is carried out in a vacuum to produce pure powders or in a hydrogen atmosphere in a graphite-tube furnace to produce technical-grade borides.

5. Fused-Salt Electrolysis: The fusion electrolysis method basically consists of placing a mixture of metal oxide, boron, and other fluxes into a bath container and then heating the solid mixture to solution by means of graphite electrodes. This method is sometimes used when the potentials and

other characteristics of the ions of a material make it difficult or impossible to synthesize by reduction with carbon or other methods.

Electrolysis is carried on at a temperature slightly above the melting point of the electrolyte. The electrolyte is usually a fluoride compound, which also acts as a flux. The final boride product being heavier than the fused electrolyte precipitates out. The fused electrolyte is then poured out, and the precipitated products are washed with  $H_2O$  and dilute  $HCl$ .

This method is best suited to the large scale production of diboride powders of commercial purity directly from naturally occurring raw materials. Fusion electrolysis is considered inefficient for most practical applications because of high electrical power cost and the fact that further processing of the final product is required. Another problem associated with this method is the inability to control the metal: boron ratio of the deposited material.

The first work on this method was performed by Andrieux (8), and later investigated by Sindeband (38). Some work by Sindeband showed the impurities to consist of graphite, both constituents and a small excess of metal or boron.

The compositions and electrolysis conditions for producing titanium and zirconium diborides as listed by Campbell are provided in Table VI.

TABLE VI: FUSION ELECTROLYSIS OF ZIRCONIUM AND TITANIUM DIBORIDES (23)

Bath Composition	Temp( $^{\circ}C$ )	EMF Volts	Current Amp	Product
$MgO/MgF_2/2B_2O_3/1/8 TiO_2$	1000	7	20	$TiB_2$
$ZrO_2/CaF_2/2B_2O_3/1/8 TiO_2$	1000			$TiB_2$
$CaO/CaF_2/2B_2O_3/1/8 ZrO_2$				$ZrB_2$ (99.6%)

6. Chemical Vapor Deposition: This method produces borides in massive form or as coatings, by depositing elements or compounds in the solid state from a chemical reaction of vapors onto a heated surface. This technique is sometimes referred to as "gas plating", "vapor plating" growth method or "vapor deposition". There are various aspects of interest within this method, such as direct boride deposition, codeposition, and pyrolysis. The study of pyrolytic synthesis (39), flame sprayed coatings and plasma deposition or plasma arc heating are new areas of ceramic technology which are closely related to this concept. Experimental and development studies have been performed by various agencies, primarily for defense use purposes, on refractory borides for coatings. Since the primary purpose of this report is concerned with diborides as a structural material no further discussion will be performed on coatings.

Massive deposits prepared by this technique are built up atom-by-atom, thereby providing a potential of preparing borides of near-theoretical density.

Rocket nozzles and other re-entry surfaces can be obtained by proper control of the deposition conditions. Chemical vapor deposition technique may be used to prepare high purity ceramics, or to form ceramic materials at temperatures below those required in conventional technology. It may also be used in filling voids in porous bodies. Disadvantages of the vapor deposition technique is the difficulty in controlling the metal: boron ratio and in the forming of large or complex shapes.

Only small amounts of borides of high purity are presently prepared by the direct decomposition of the halides of the metals and boron. The halide gases are mixed with hydrogen and decomposed at temperatures around 1100 to 1200°C, on inert wires or on wires of the specific metal. The metal and the boron deposit simultaneously from the vapor phase and form the diboride. This direct deposition method was first used by Moers (6) and studied later by Walther (40). Powell, Campbell, and Gonser (41), VanArkel (42) and Becker (10) have reviewed the early work.

Two recent investigations concerning gas phase reactions which were not directly associated with diborides, but could very likely be used for producing them, are studies by Stanford Research Institute (32), and Arthur D. Little (43). Abstracts of both these studies are available in Appendix I.

The Stanford effort was a plasma-arc heating system. The major limitation in synthesis was the wide range of thermal history of the collected materials. The variation in degree of heating was caused by particle size differences and effect of plasma impinging on previously deposited materials, new phases which occur as a result of gas-gas interactions are considerably diluted by unreacted material.

The Arthur D. Little investigation was primarily a development of vapor deposition apparatus for obtaining temperatures above 1700°C and producing shapes of 4 by 8 in sizes. They showed feasibility of directly depositing zirconium and hafnium diborides by thermal decomposition of the corresponding borohydrides.

The optimum deposition temperatures for the various metal borides of interest have been listed by Campbell, et al, (44) as follows: titanium-boride (1000-1300°C, 1830-2730°F), zirconium boride (1700-2500°C, 3090-4530°F), hafnium boride (1900-2700°C, 3450-4890°F), vanadium boride (900-1300°C, 1650-2370°F), tantalum boride (1800-2000°C, 3270-3630°F), chromium boride (1200-1600°C, 2190-2910°F). Raising the deposition temperature and reducing the concentration of halides in the vapor promotes the development of coarse grains in the product. Increasing the deposition rate with high halide concentrations or lowering the substrate temperature causes the precipitation of a fine-grained material. In both cases, the product seems to be purer than original volatile compounds. Since a great deal of the recent work on vapor deposition has been on highly anisotropic BN or C, some means of comparing or relating them with the borides is essential. Unfortunately, it appears that they are basically different, in that borides do not possess the stacking advantages of highly anisotropic materials. Therefore, the vapor-deposited TiB<sub>2</sub> and ZrB<sub>2</sub> in massive form will probably not show a significant difference in properties from

hot pressed products. Advantages that might be expected from material precipitated from the vapor are listed:

1. High density and resistance to oxidation.
2. Forming dense borides in shapes that are not readily adaptable to hot pressing.
3. Produce a ultra fine powder for rapid densification on hot pressing.

In codeposition there exists the potential of forming two phase systems having a more intimate dispersion of the two phases than can be formed by normal ceramic techniques. This method consists of depositing the diborides from a mixture of halide vapors which contain the same halogen. The practicality of preparing such materials in massive form for large scale use is presently questionable.

Depositing borides by the thermal decomposition of the corresponding metal borohydride has been performed with titanium, zirconium, and hafnium. The vaporization temperatures required for these materials were listed by Campbell (23) as follows:

Ti(BH <sub>4</sub> ) <sub>3</sub> :	-20 to /25°C
Zr(BH <sub>4</sub> ) <sub>4</sub> :	-20 to /25°C
Hf(BH <sub>4</sub> ) <sub>4</sub> :	-30 to /25°C
Th(BH <sub>4</sub> ) <sub>4</sub> :	150 to 200°C

The deposition temperatures range around 200 to 300°C. These compounds deposit more readily at reduced pressure. This method is not suitable for large scale production, since most of the borohydrides decompose, to some extent, at room temperature.

7. Single Crystals: The most recent studies performed with diboride crystals is of primary concern in this report. The two investigations of most recent interest were performed by Kiffer (30) and Lynch, et al (45). Abstracts of both these reports is found in Appendix II. These two studies deal with TiB<sub>2</sub>. A study is presently being performed by Arthur D. Little under an Air Force contract concerning some refining methods for producing single crystals of ZrB<sub>2</sub> and HfB<sub>2</sub>. General information concerning earlier work of single diboride crystals can be obtained in references 22 and 23.

The objective of the investigation by Kiffer was to produce single crystals in sizes suitable for property measurement. The sizes were to be at least 1/4 inch diameter and 1/2-inch long. No reports on the preparation of this size crystal were found in the literature. A proprietary method was developed for growing TiB<sub>2</sub> crystals. The method was similar to the Verneuil method in that the powdered raw material, in a hot gas stream, is deposited on the molten surface of the crystal being grown. A arc heat source was used instead of the usual combustion type. The growing crystal was shielded from surroundings with argon. The growing crystal, or boule, was a cylinder and oriented so that



the axis was vertical. The top of the crystal was kept molten by a flame impinging on it. Growth occurs when a supply of powdered raw material passes through the flame onto the molten surface.

The powders usually used for growing new crystals by the Verneuil technique were specially prepared. The particle size must be controlled to avoid nucleation of new grains and to produce a uniform dispensing material. In view of this,  $TiB_2$  powder used was synthesized directly from the elements. The titanium was minus 200 mesh powder purchased from Union Carbide Metals Company. The boron was crystalline powder (greater than 99% boron), minus 100 mesh, purchased from U. S. Borox and Chemical Corporation.

The single crystal pieces obtained from this method contained 67.4 weight percent and 69.1 percent titanium, 30.7 and 30.9 percent boron. Stoichiometric  $TiB_2$  contains 68.88 percent by weight titanium and 31.12 percent boron.

The investigation undertaken by Lynch, et al., of the Directorate of Materials and Processes at Aeronautical Systems Division was to determine and develop the best possible methods and techniques of sectioning, mounting, grinding, polishing, and etching of single-crystal and polycrystalline  $TiB_2$ . This report is the first one that presents metallographic techniques and procedures to characterize the diborides and establish a basis for future development work. All the specimens used were supplied by the Linde Company.

The techniques determined by this investigation to be the best for mechanical preparation of  $TiB_2$  crystals is shown as reported in Figure 2.

The best etchants were determined to be a solution of 5 parts concentrated  $H_2SO_4$ , 5 parts concentrated  $HNO_3$ , and 4 to 10 parts distilled  $H_2O$ ; or for the electrolytic method a mixture of 6 parts methanol to 1 part concentrated  $H_2SO_4$ .

8. Procurement of High Purity Diborides: Air Force Contract 33(657)-8635 initiated on 4 May 1962 by Manlabs, Incorporated of Cambridge, Massachusetts was to investigate boride compounds for very high temperature applications. The selected information provided in this report was obtained from all data sheets solicited by Manlabs at the time this report was written. Tables VII - XI summarize the procurement information available at that time.

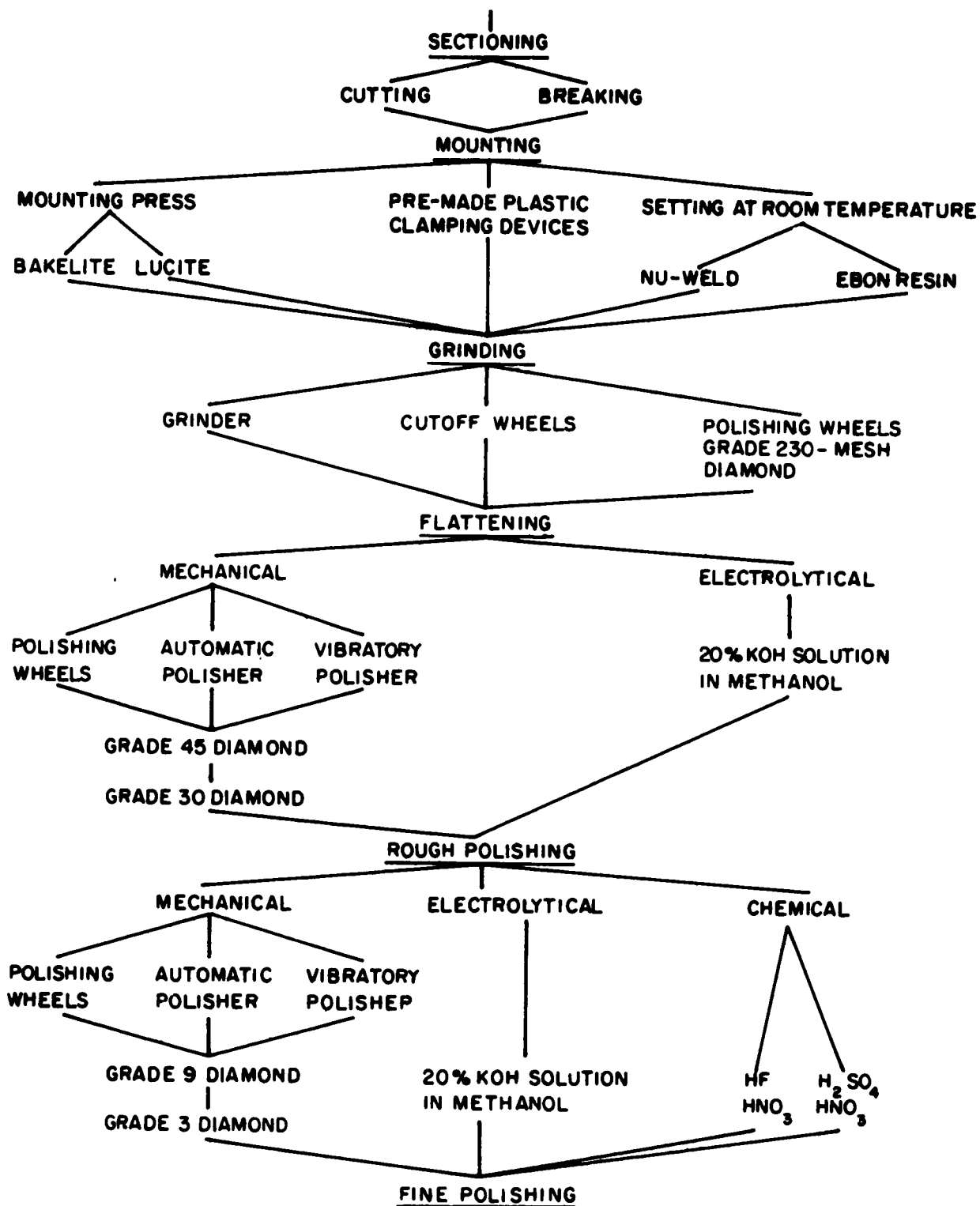


Figure 2. Schematic of Metallurgical Procedure for  $TiB_2$  (Ref 45)

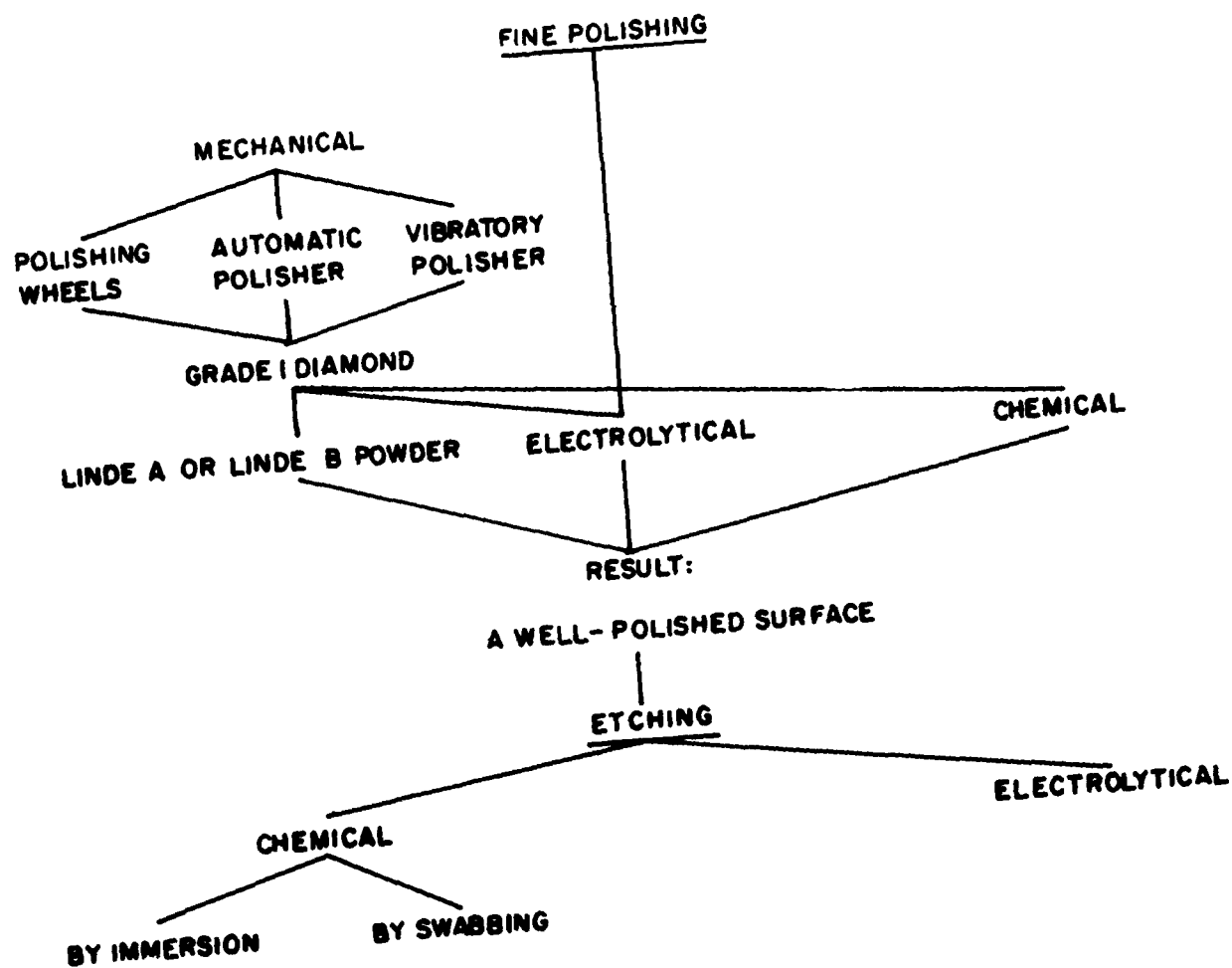


Figure 2. (Cont'd) Schematic of Metallographic Procedure for  $TiB_2$  (Ref 45)

TABLE VII: PROCUREMENT SOURCES FOR  $TiB_2$ 

Source	Purity %	Particle Size		Cost
		Microns	Mesh	
American Potash & Chemical Co 99 Park Avenue New York 16, New York	99.1	6-12		\$15/lb 1-4 lbs \$12/lb 5-24 lbs
U. S. Borax & Chemical Co Research Laboratory New Products Development Dept 412 Cresent Way Anaheim, California	99.4 <del>4</del> .3	5-10		\$10.50/lb 0-20 lbs
Kawecki Chemical Company 22 East 42nd Street New York 17, New York	99.5		-325	\$11.50/lb
Cooper Metallurgical Co Cleveland, Ohio	99.2		-80	\$181.00/lb
Millmaster Chemical Corp 99 Park Avenue New York 16, New York	99.5		-325	\$14.00/lb

TABLE VIII: PROCUREMENT SOURCES FOR  $ZrB_2$ 

Source	Purity %	Particle Size		Cost
		Microns	Mesh	
U. S. Borax & Chemical Co Research Laboratory New Products Development Dept 412 Cresent Way Anaheim, California	97.7 <del>7</del> 0.2	5-10		\$10.50/lb 0.20 lbs
Carborundum Company New Products Division Niagara Falls, New York	96.83			\$85.00/lb 2.0 lbs
Cooper Metallurgical Co Cleveland, Ohio	98.84		-80	\$295.00/lb
Millmaster Chemical Corp 99 Park Avenue New York 16, New York	97.55	3-5		\$25.00/lb

TABLE IX: PROCUREMENT SOURCES FOR NbB<sub>2</sub>

Source	Purity %	Particle Size		Cost
		Microns	Mesh	
U. S. Borax & Chemical Co Research Laboratory New Products Development Dept 412 Cresent Way Anaheim, California	99.99	10-15		\$105.00/lb 20 lbs
Kawacki Chemical Company 22 East 42nd Street New York 17, New York	99.99			\$105.00/lb
Cooper Metallurgical Co Cleveland, Ohio	99.32		-100	\$454.00/lb
Millmaster Chemical Corp 99 Park Avenue New York 16, New York	98.5			\$100.00/lb

TABLE X: PROCUREMENT SOURCES FOR TaB<sub>2</sub>

Source	Purity %	Particle Size		Cost
		Microns	Mesh	
U. S. Borax & Chemical Co Research Laboratory New Products Development Dept 412 Cresent Way Anaheim, California	99.99	10-15		\$70.00/lb 20 lbs
Kawacki Chemical Company 22 East 42nd Street New York 17, New York	99.99			\$70.00/lb
Cooper Metallurgical Co Cleveland, Ohio	99.36		-100	\$454.00/lb
Millmaster Chemical Corp 99 Park Avenue New York 16, New York	99.00			\$81.00/lb

TABLE XI: PROCUREMENT SOURCES FOR  $\text{HfB}_2$ 

Source	Purity %	Cost
Carborundum Company New Products Division Niagara Falls, New York	97.34	\$420.00/lb
Wah Chang 233 Broadway New York, New York	99.55	\$650.00/lb

## IV. PROPERTIES

General: The information contained in this section is based primarily on diborides of the transition metals. A detailed knowledge of properties of these materials is lacking. The literature points out the insufficiency of property data concerning the borides. The transition group of diborides are characterized by the properties listed below:

1. High melting point.
2. Extreme hardness.
3. High thermal conductivity.
4. High electrical conductivity.
5. Corrosion resistance similar to the carbides and silicides.
6. Soluble in fused alkalis.
7. Considerable solubility in acids, especially nitric acid.
8. Stable in the presence of carbon;  $\text{ThB}_2$  is unstable.
9. Oxidation resistance at high temperature is nothing exceptional.
10. None of the diborides is a superconductor (63-64).
11. All diborides except  $\text{ZrB}_2$  are weakly paramagnetic (65).

The structure of the diborides of groups 4A, 5A, and 6A of the periodic classification is similar to that of graphite. These borides have alternate layers of metal and boron atoms normal to the c-axis, each metal atom having twelve equidistant boron neighbors. The boron plane consists of atoms in a hexagonal arrangement.

Data on the high temperature stability of the borides is scarce, but investigations by Kiessling (14) indicated that borides of the transition elements are similar to the hydrides, carbides, and nitrides of these elements, in which stability decreases with increasing atomic number of the transition element within the period. Borides are more resistant to oxidation than the above types of materials. They resist oxidation up to  $1200^\circ\text{C}$ - $1300^\circ\text{C}$  ( $2192^\circ\text{F}$ - $2372^\circ\text{F}$ ) in air, although superficial oxidation occurs at lower temperatures. Vanadium diboride is oxidized appreciably at  $1000^\circ\text{C}$  to  $1100^\circ\text{C}$  ( $1832^\circ\text{F}$ - $2012^\circ\text{F}$ ) and tantalum borides at  $1100^\circ\text{C}$  to  $1200^\circ\text{C}$  ( $2012^\circ\text{F}$ - $2192^\circ\text{F}$ ). Zirconium diboride is fairly resistant up to  $1300^\circ\text{C}$  or  $1400^\circ\text{C}$  ( $2372^\circ\text{F}$ - $2552^\circ\text{F}$ ), and titanium diboride up to  $1400^\circ\text{C}$  or  $1500^\circ\text{C}$  ( $2552^\circ\text{F}$ - $2732^\circ\text{F}$ ), although some oxide film is

formed at these higher temperatures (43). Chromium borides is reported to resist oxidation at high temperatures.

The strength-weight ratio of  $TiB_2$  is not exceeded by any other bulk material from  $1600^\circ C$  ( $2912^\circ F$ ) to above  $2000^\circ C$  ( $3632^\circ F$ ) (43). Very little information on tensile, compressive, bending, impact and stress rupture strength is available.

A few of the values which are available include the flexural strength of titanium diboride (96 percent theoretical density) which has been reported to be 35,000 psi from  $25^\circ C$  to  $2000^\circ C$  ( $77^\circ F$ - $3632^\circ F$ ) with a modulus of elasticity of  $60 \times 10^6$  psi. The compressive strength has been reported as 97,000 psi at room temperature. For zirconium diboride modulus of rupture values are reported from 8,000 to 29,000 psi at room temperature, with a tensile strength of 28,700 psi and a modulus of elasticity of  $50 \times 10^6$  psi (43).

No systematic search of the thermal shock properties of the borides has been performed. The thermal and mechanical characteristics of the borides indicate they might have relatively good thermal shock resistance when compared with other ceramic materials.

In general, data has been obtained on products processed by molding and sintering or by hot-pressing. The purity is generally greater than 97 percent but very little study has been completed on high-purity materials.

The property data recorded on the following pages includes only information available in the literature concerning all types of properties of specific diboride binary compounds and thorium tetraboride. The variation of properties as published is explained by the fact that most of the data is of measurements with incomplete background on purity, porosity, and heat treatment. Unfortunately the reliability of the data is difficult to estimate but nevertheless is interesting and possibly of some value as a guide for the materials engineer.

#### Thermal Properties:

TABLE XII: MELTING POINTS

Material	Melting Points in Degrees Centigrade				
	(22)	(66)	(67)	(43)	(26)
$TiB_2$	2980	2920/5	2900	2900	2980
$ZrB_2$	2680	2680/5	3050	3040	3040
$HfB_2$	3100	3240/5	3240	3000	3250
$VB_2$	2100/60	2350/5	2400	2100	2400
$NbB_2$	2900	3050/5	3050	2900	3000
$TaB_2$		3200/5	3200	3000	3100
$CrB_2$	1850	1900/5	2150	1850	2200
$TaB_4$	2500				

TABLE XIII: TABULATION OF MELTING POINTS OF DIBORIDES\*

Material	High		Low	
	Degrees C	Degrees F	Degrees C	Degrees F
TiB <sub>2</sub>	2980	5395	2900	5250
ZrB <sub>2</sub>	3050	5520	2680	4855
HfB <sub>2</sub>	3250	5880	3000	5430
VB <sub>2</sub>	2400	4350	2100	3810
NbB <sub>2</sub>	3050	5520	2900	5250
TaB <sub>2</sub>	3200	5790	3000	5430
CrB <sub>2</sub>	2280	4135	1850	3360
ThB <sub>4</sub>	2500	4530	—	—

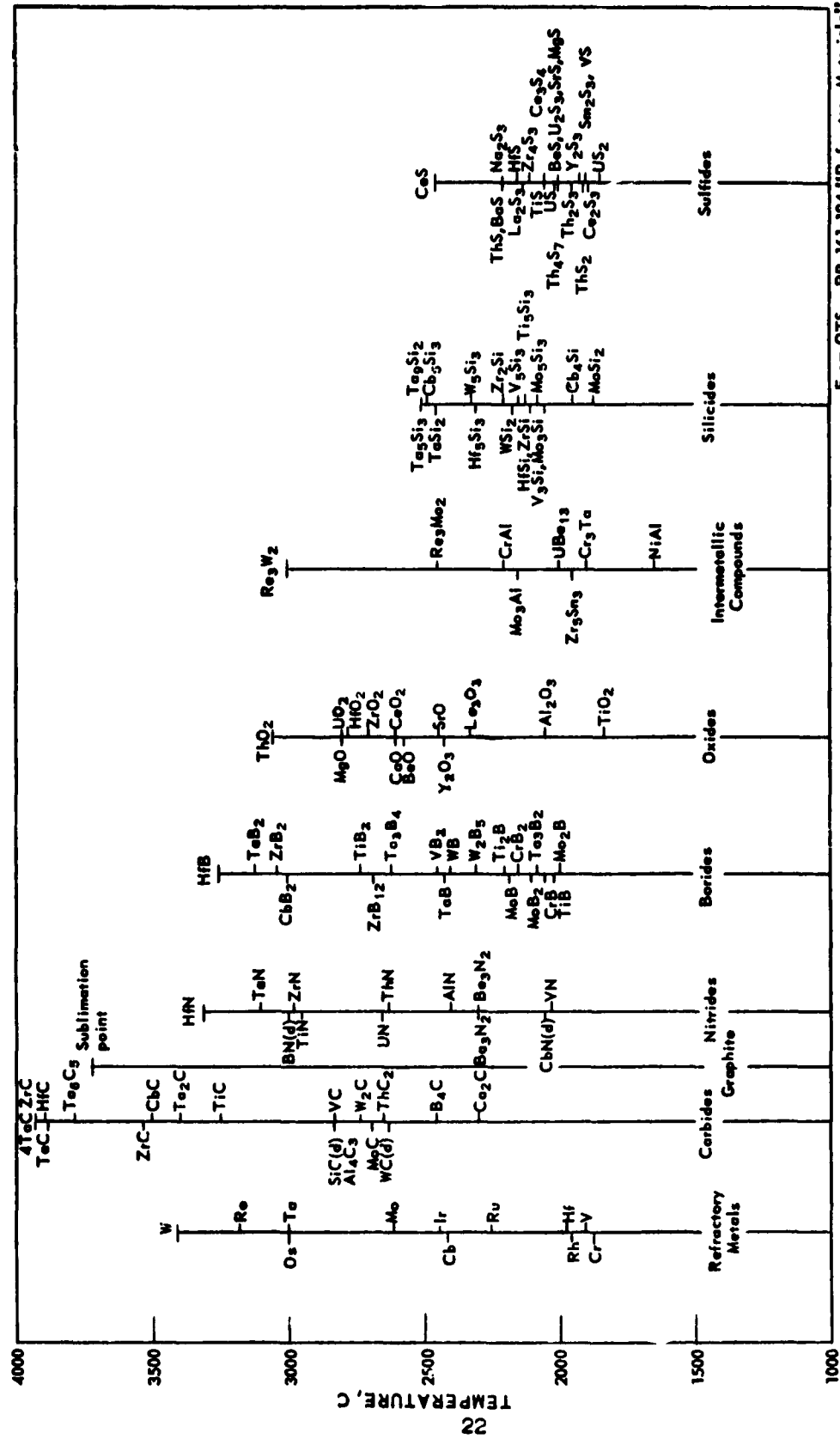
\*Values represent high and low sides of a range as recorded in Table XII.

TABLE XIV: THERMAL EXPANSION (26)

Diboride	Temperature Range	Expansion ( $\times 10^{-6}$ per C)		
		Average *a	*b	Specific Average
ZrB <sub>2</sub>	rm-1000°C (1830°F)			5.5
	0-1200°C			6.63
TiB <sub>2</sub>	0-1200°C	5.5	5.1	
HfB <sub>2</sub>	0-1200°C			5.8
VB <sub>2</sub>	0-1200°C			7.5
NbB <sub>2</sub>	0-1200°C	7.9	8.3	
TaB <sub>2</sub>	0-1200°C			5.12
CrB <sub>2</sub>	0-1200°C			11.1

\*Directions of the a and c axes.





**Figure 3. \*Comparison of Boride Melting Points with other Refractory Materials**

**From OTS - PB 161 194 "Refractory Materials"**

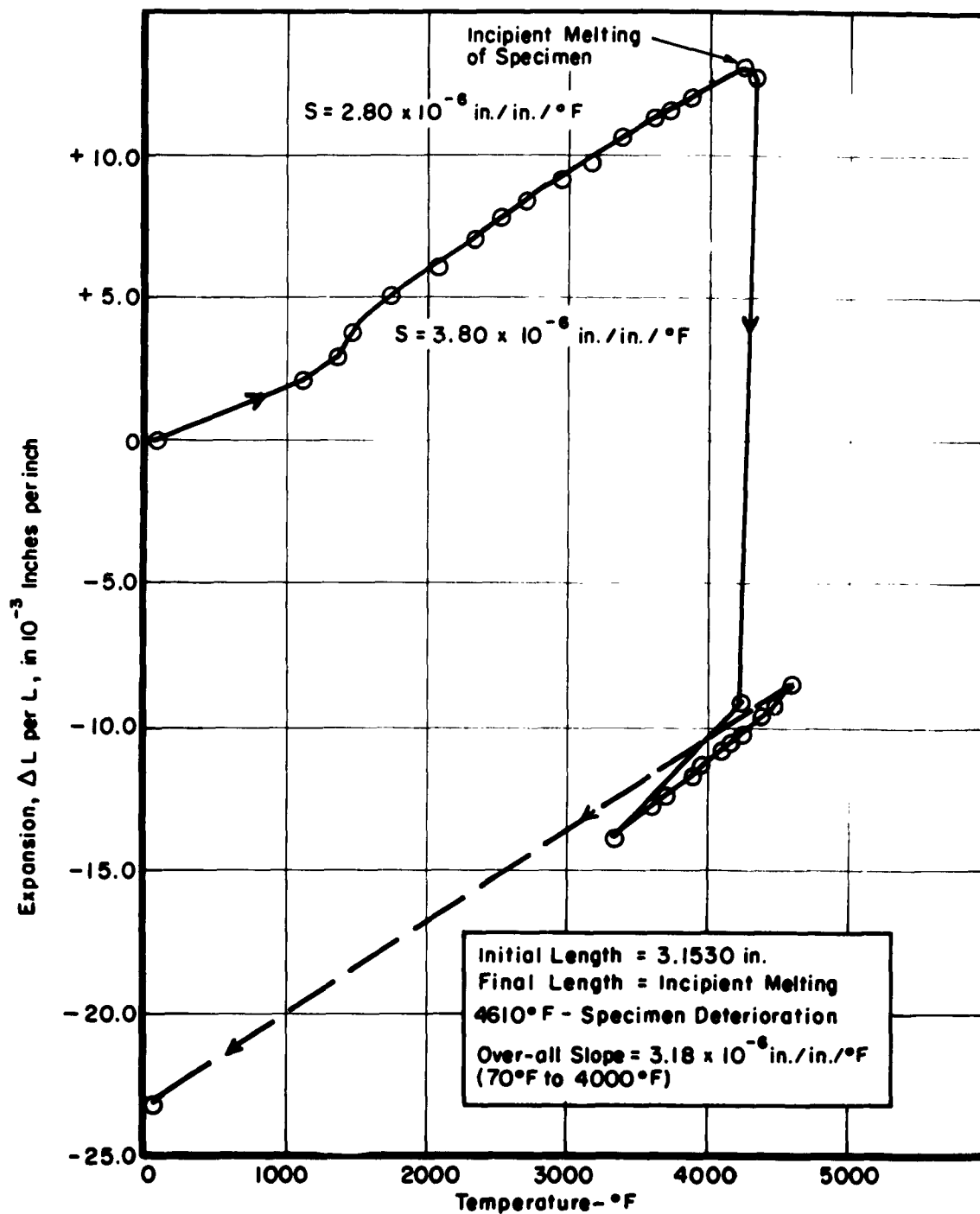


Figure 4. Thermal Expansion of Tantalum Diboride (Ref 83)

Specimen supplied by General Electric Company. Pressed and sintered 96.5% of theoretical density, density equals 12.15 g/cm<sup>3</sup> 3/4" diameter x approximately 3" length. Test method: graphite tube dilatometer.

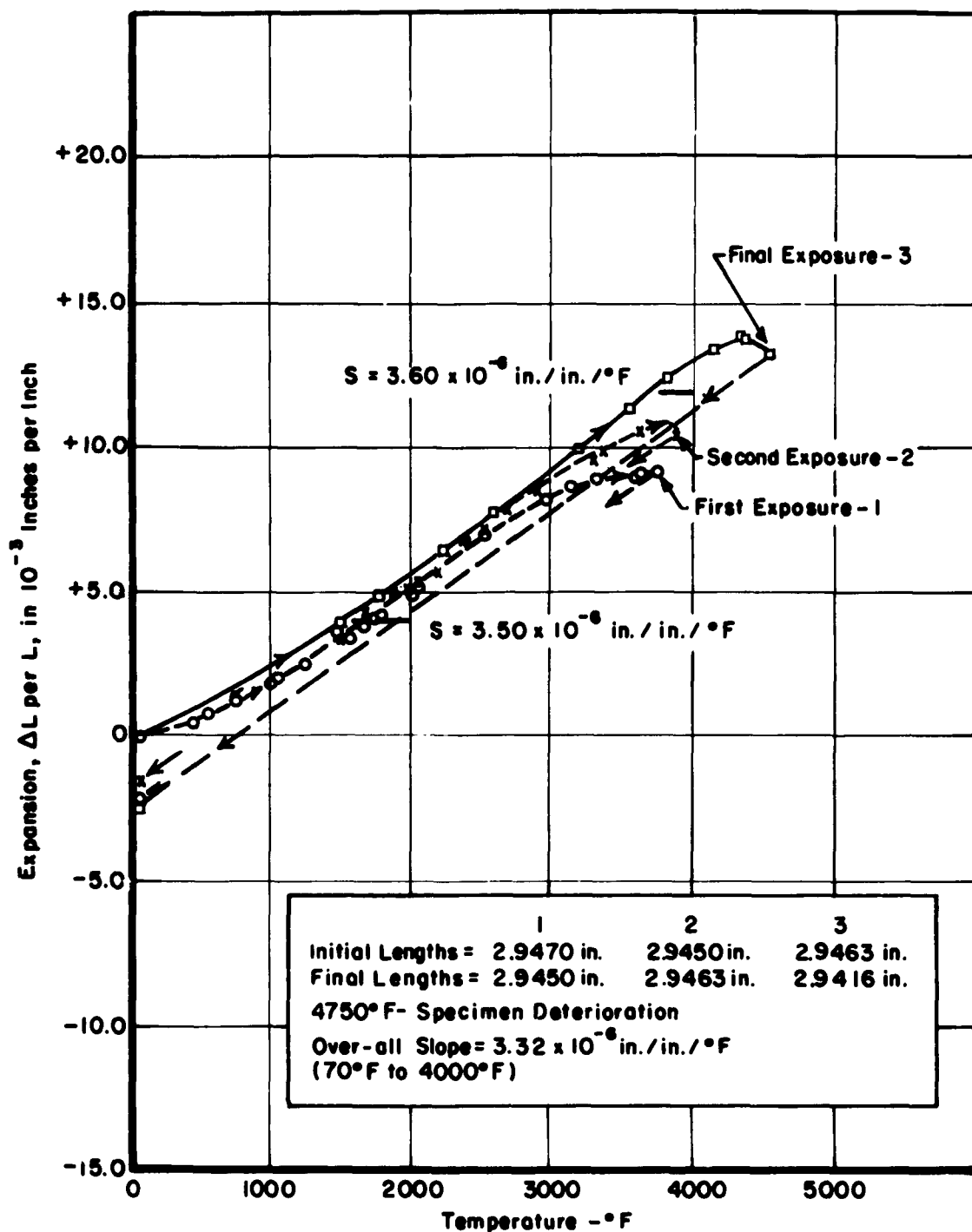


Figure 5. Thermal Expansion of Zirconium Diboride (Ref 83)

Specimen supplied by Norton Company, Hot pressed, 70-75% of theoretical density, density equals 4.14 g/cm, 3/4" diameter x approximately 3" length. Test method: graphite tube dilatometer.

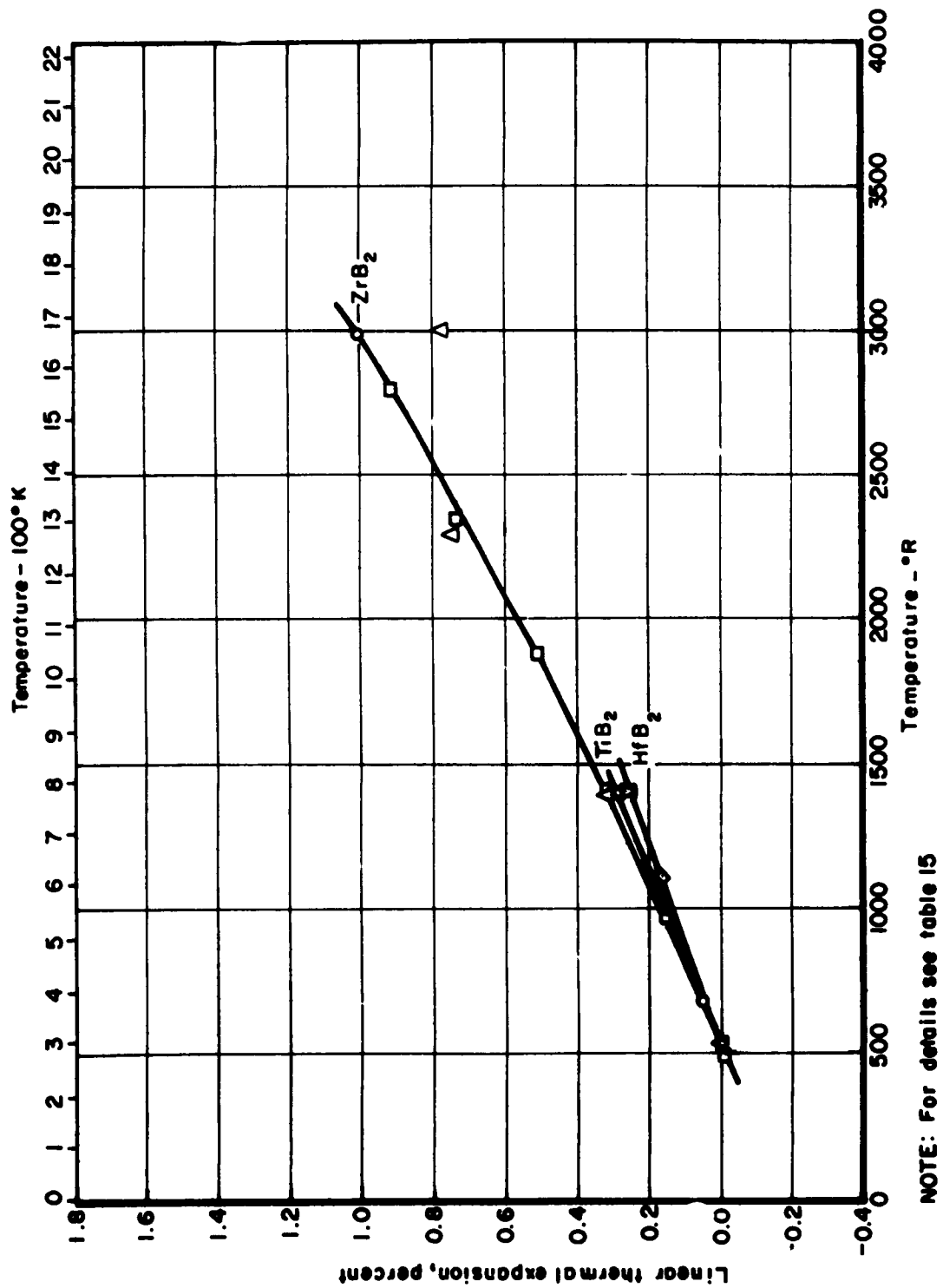


Figure 6. Thermal Expansion ZrB<sub>2</sub>, HfB<sub>2</sub> and TiB<sub>2</sub> (Ref 85)

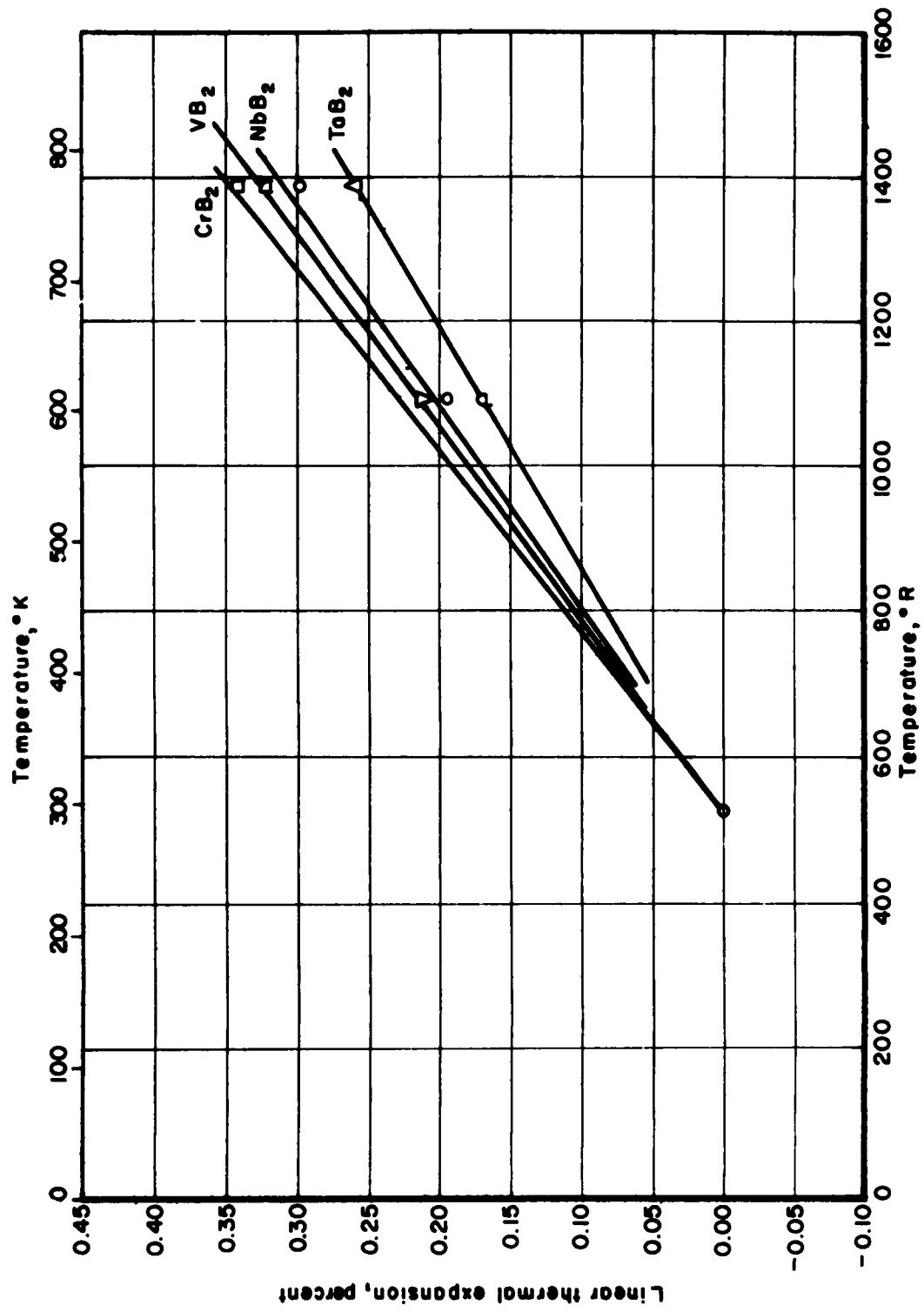


Figure 7. Thermal Expansion of CrB<sub>2</sub>, NbB<sub>2</sub>, VB<sub>2</sub>, TaB<sub>2</sub> (55)

TABLE IV: THERMAL EXPANSION OF BORIDES (85)

Symbol	Investigator	Material Composition	Test Method	Remarks
○	Binder, I. and Moskowitz, D	CrB <sub>2</sub>	X-ray diffraction with Morelco gel-counter spectrometer	Avg. of measurements made in the c and a direction of the unit cell
□	Ibid.	CrB <sub>2</sub>	Dilatometer	
▽	Ibid.	NbB <sub>2</sub>	Same as above	Same as 0
◊	Ibid.	NbB <sub>2</sub>	Dilatometer	
◻	Ibid.	TaB <sub>2</sub>	X-ray diffraction with Morelco gel-counter spectrometer	Same as 0
◻	Ibid.	TaB <sub>2</sub>	Dilatometer	
◻	Ibid.	VB <sub>2</sub>	X-ray diffraction with Morelco gel-counter spectrometer	Same as 0
◻	Ibid.	VB <sub>2</sub>	Dilatometer	

TABLE IV: THERMAL EXPANSION OF BORIDES (85) (CONTINUED)

Symbol	Investigator	Material Composition	Test Method	Remarks
○	Mesrop, V. S. and Sameonov, G. V.	ZrB <sub>2</sub>	Not given	Sintered 30 min. at 1400 C in He atmos.
□	Moser, F. A. and Bols, L. H.	ZrB <sub>2</sub> / 4% Hf	X-ray diffraction	Hot pressed
△	Crandall, W. B. and Lawrence, W. G.	ZrB <sub>2</sub>	Self-calibrating	
◇	Binder, I. and Moskovits, D.	ZrB <sub>2</sub>	X-ray diffraction	
▽	Ibid.	ZrB <sub>2</sub>	Dilatometer	
◊	Ibid.	HfB <sub>2</sub>	X-ray diffraction	
◻	Ibid.	HfB <sub>2</sub>	Dilatometer	
○	Mesrop, V. S. and Sameonov, G. V.	TiB <sub>2</sub>	Not given	
□	Binder, J. and Moskovits, D.	TiB <sub>2</sub>	X-ray diffraction	
△	Ibid.	Same as above	Dilatometer	

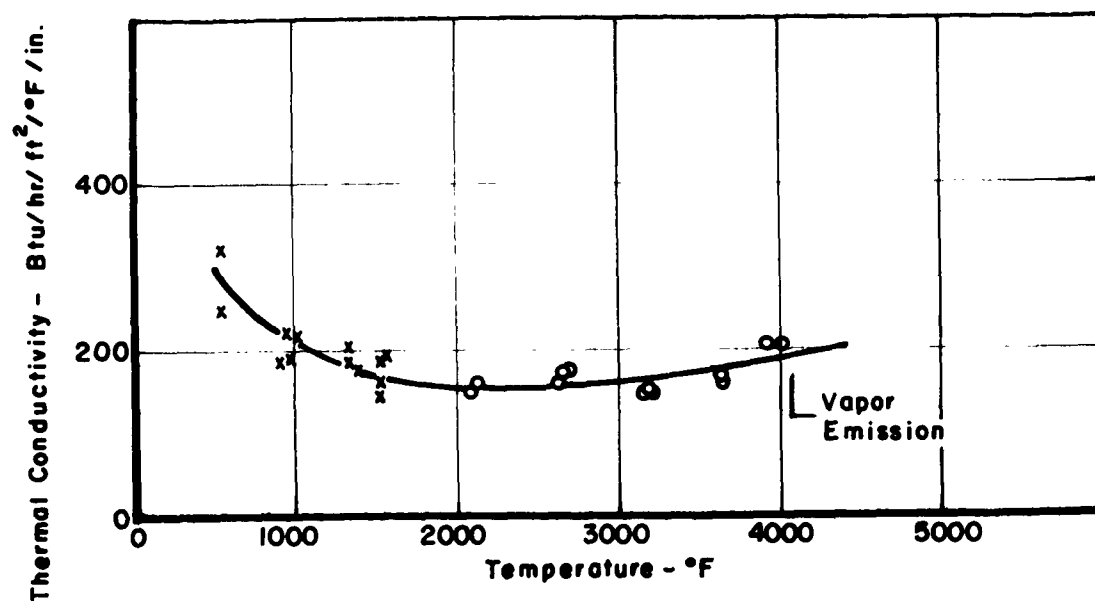


Figure 8. Thermal Conductivity of Zirconium Diboride (Ref 83)

Specimen supplied by Norton Company. Hot pressed, 70-75% of theoretical density, density equals 4.14 g/cm<sup>3</sup>, 3/4" diameter x approximately 3/4" length. Test method: Radial heat flow calorimeter.



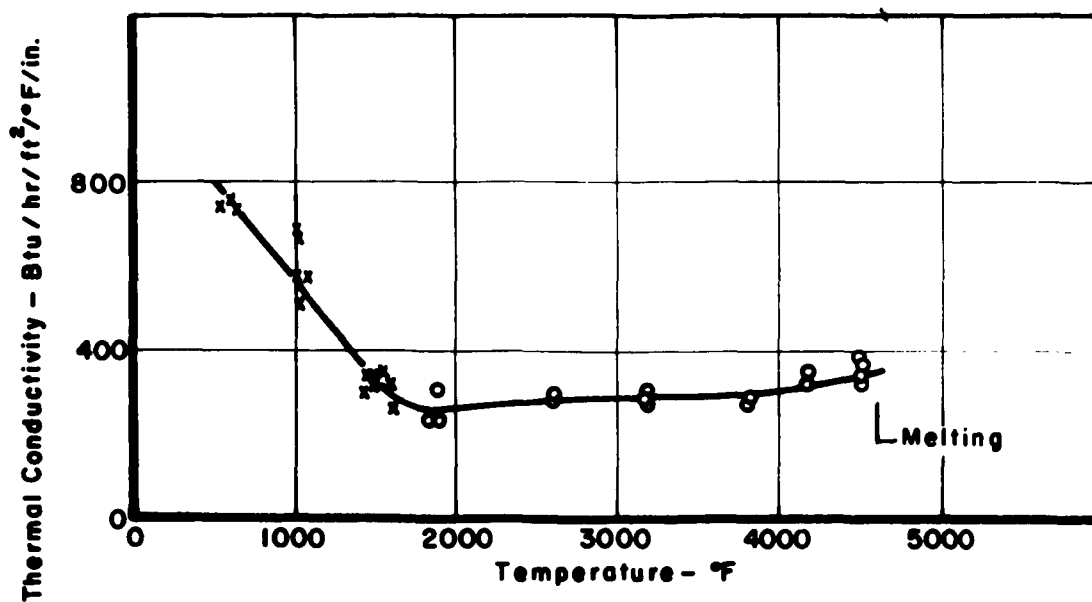


Figure 9. Thermal Conductivity of Tantalum Diboride (Ref 83)

Specimen supplied by General Electric Company. Pressed and sintered, 96.5% of theoretical density, density equals 12.15 g/cm, 3/4" diameter x approximately 3/4" length. Test Method: Radial heat flow calorimeter.

TABLE XVI: THERMAL CONDUCTIVITIES

Diboride	Temperature		Conductivity		Reference
	(°C)	(°F)	Cal sec <sup>-1</sup> , cm <sup>-2</sup> , cm °C <sup>-1</sup>	*BTU/hr/ft <sup>2</sup> /°F/inch	
TiB <sub>2</sub>	23	73.4	0.058	168.2	26,71
TiB <sub>2</sub>	200	392	0.063	183.0	71
ZrB <sub>2</sub>	23	73.4	0.058	168.2	26,71
ZrB <sub>2</sub>	200	392	0.055-0.060	159.6-174.1	71
NbB <sub>2</sub>	23	73.4	0.040	116.0	26,43,71
NbB <sub>2</sub>	200	392	0.047-0.062	136.3-180.0	71
TaB <sub>2</sub>	20	68	.026	75.5	26,43
CrB <sub>2</sub>	20	68	.076	222.0	26

\*Slide rule calculations using the conversion factor; to convert from calories, gram (15°C)/sec.cm<sup>2</sup>/cm to btu(mean)/hr ft<sup>2</sup>/inch, multiply by 2902.9 as given in Lange's Handbook of Chemistry, 8th edition, 1952.

TABLE XVII: HEAT CAPACITY\* (26)

Diboride	Heat Capacity C 10 <sup>3</sup> , cal/gram degree
TiB <sub>2</sub>	151
ZrB <sub>2</sub>	120
HfB <sub>2</sub>	60
VB <sub>2</sub>	160
NbB <sub>2</sub>	100
TaB <sub>2</sub>	58
CrB <sub>2</sub>	112

\*Nonporous specimens.

**Thermal Shock Resistance:** Very little data is available in the open literature on thermal shock resistance of binary diboride compounds. To improve thermal shock resistance the nitrides of boron or silicon which possess high thermal shock resistance, are recommended by Samsonov (26) to be added to the diborides in quantities no smaller than 15 percent.

# Crystal Structure:

TABLE XVIII: CRYSTAL STRUCTURES AND LATTICE PARAMETERS

Boride	Form	Metal-Boron Spacing, Å <sup>o</sup>	Lattice Constants, Å <sup>o</sup>		c/a	Reference
			a	c		
ZrB <sub>2</sub>	*Hexagonal AlB <sub>2</sub> (C-32)	2.54	3.169-3.170	3.528-3.533	1.11	14,22,26,68 78
TiB <sub>2</sub>	*Hexagonal AlB <sub>2</sub> (C-32)	2.38	3.028 3.026	3.228 3.213	1.06	22,26,68 14,74
CrB <sub>2</sub>	*Hexagonal AlB <sub>2</sub> (C-32)	2.29	2.969	3.066		14,22,26,68
HfB <sub>2</sub>	*Hexagonal	2.51	3.14 ± 0.002 3.14	— 3.47	1.10	22,26,68,69
NbB <sub>2</sub>	*Hexagonal AlB <sub>2</sub> (C-32)	2.43	3.089 3.086	3.303 3.306	1.07	14,22,26,68
TaB <sub>2</sub>	*Hexagonal AlB <sub>2</sub> (C-32)	2.41	3.078 3.088 3.099 (metal-rich) 3.057 (boron-rich)	3.265 3.241 3.224 3.291	0.62	14,15,26,68
VB <sub>2</sub>	*Hexagonal AlB <sub>2</sub> (C-32)	2.27	2.998 3.006	3.057 3.056	1.02	14,22,26,68
TbB <sub>4</sub>	Tetragonal Space Group D <sub>4h</sub>	5-P <sub>4</sub> /nm	7.256	4.113		68,76

\* See Figure 10

# Mechanical Properties:

\*TABLE XIX: DENSITY

Boride	Form or Measurement Technique	Density g/cm <sup>3</sup>	Reference
ZrB <sub>2</sub>	Theoretical	6.1 6.085-6.17 6.2	22,33,43 72 27
TiB <sub>2</sub>	Pressed and Sintered Theoretical	4.04-3.31 4.50-4.52 4.40	34** 22,33,72 43
VB <sub>2</sub>	X-ray Fused-salt electrolysis	4.61 5.1 5.28	15 22 8,43

\*Continued on page 34.

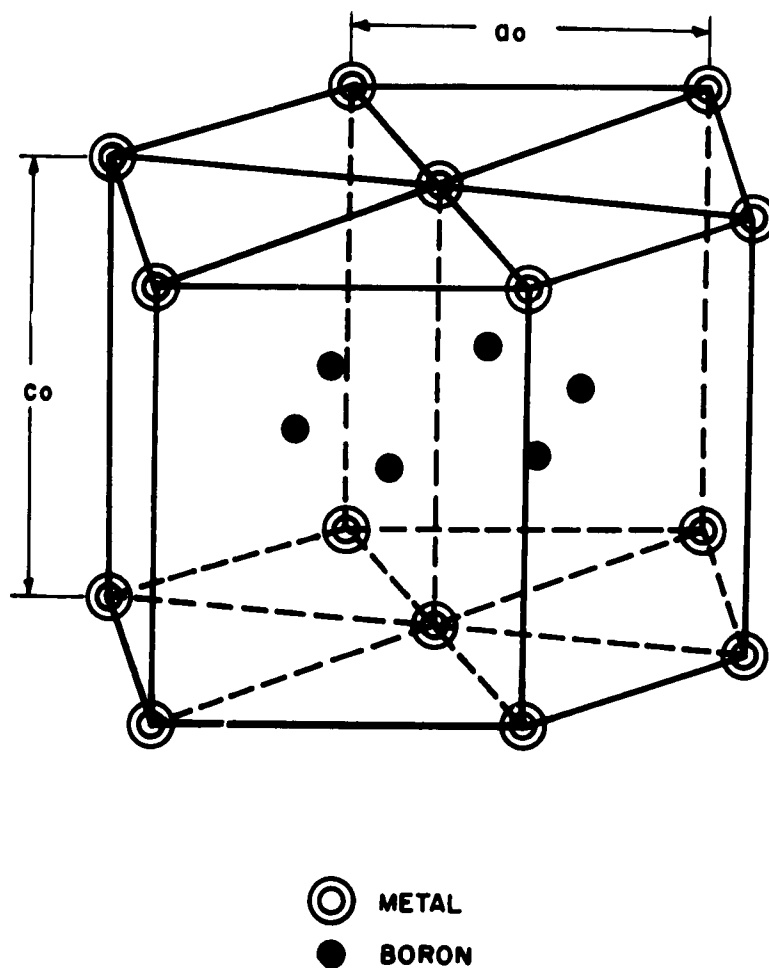


Figure 10. Diboride Structure ( $MB_2$ )

The structure is of the  $C32$  type, space group  $D'6h - C6mm$ , with metal atoms, at  $0,0,0$  and boron atoms at  $1/2, 2/3, 1/2$  and  $2/3, 1/3, 1/2$ . The unit cell contains one molecule of  $MeB$ . This structure corresponds to alternate layers of metal and boron atoms, parallel to the basal plane of the lattice. As the metal atom size increases, both  $a$  and  $c$  dimensions of the lattice increase and the axial ratio also increases slightly.

TABLE XIX: DENSITY (CONTINUED)

Boride	Form or Measurement Technique	Density g/cm <sup>3</sup>	Reference
NbB <sub>2</sub>	X-ray	6.4-6.60 7.21	15 22,43
TaB <sub>2</sub>	Pycnometrically	11.0-11.70	15
	X-ray (theoretical)	12.6	22,43
CrB <sub>2</sub>	X-ray	5.6	22,43
ThB <sub>4</sub>	X-ray	8.45	
HfB <sub>2</sub>	X-ray (theoretical)	11.2	2,43
	Pycnometrically	10.5	2

\*\*Pressed zirconium diboride powders (2 to 3 microns) particle size showed a minor density increase at the temperature up to 2200°C, and a major increase above 2100°C to 2400°C.

TABLE XX: HARDNESS

Diboride	Form	*Hardness	Reference
ZrB <sub>2</sub>	Hot pressed	1560 (K-100, KHN) 8 (Mohs) 2200 (VPH)	72 22
		2250 (VPH)	26
		2300 (VPH)	27,68
TiB <sub>2</sub>	Hot pressed	2710 (K-100, KHN) 9 (Mohs) 3370 (VPH)	72 22 26,27,68
VB <sub>2</sub>		8-9 (Mohs) 2800 (VPH)	22 26
		2070 (VPH)	27,68
NbB <sub>2</sub>		48 (Mohs) 2600 (VPH)	22 26
		2200 (VPH)	27,68
TaB <sub>2</sub>		2500 (VPH)	26,27,68
CrB <sub>2</sub>		1800 (VPH)	26,27,43, 68
HfB <sub>2</sub>		2900 (VPH)	26

\*K-100 - 100 gram load

KHN - Knoop hardness number

VPH - Vickers microhardness, Kg/mm<sup>-2</sup> (30-50 gram load)

The microhardness technique for determination of hardness for diborides should obtain the most reliable results due to their brittleness (26).

The borides are in general the hardest of the metal like compounds (silicides, nitrides, carbides, etc.), as would be expected from the crystal structure and interatomic-bond strengths.

TABLE XXI: MICROHARDNESS AS A FUNCTION OF LOAD (26)

Diboride	Microhardness Kg/mm <sup>2</sup>	Load Grams
TiB <sub>2</sub>	3050	20
	4100	30
	3500	50
	3450	120
NbB <sub>2</sub>	4800	20
	3800	30
	3200	50
	3000	100
TaB <sub>2</sub>	2900	20
	3100	30
	2200	50
	1950	100
ZrB <sub>2</sub>	2000	120
	2000	150
	2600	20
	2100	30
	1900	50
	400	100

TABLE XXII: BENDING STRENGTH (1)

Diboride	Form	Temp (°C)	Strength PSI	Ultimate Kg/mm <sup>2</sup>	Reference
*TiB <sub>2</sub>	Hot pressed, self bonded		19,000		72,85
ZrB <sub>2</sub>	Hot pressed, self bonded		29,000		72,85
		1000		39	26
			26,000		27
CrB <sub>2</sub>				62	26

\*The flexural strength of TiB<sub>2</sub> at 96 percent of theoretical density was stated as 35,000 psi from 25°C (77°F) to 2000°C (3632°F).

TABLE XXIII: BENDING STRENGTH TiB<sub>2</sub> (84)

Temperature (°C)	Strength (psi)
RT	26,300
RT	29,500
600	55,500
800	28,400
900	31,000
900	39,000
1000	39,500
1010	34,600
1200	32,000
1300	35,100

These figures do not reflect the true strength of the material, due to the considerable amount of oxidation that occurred to the specimens. Specimens were approximately 1.0" x 0.4" x 0.2", and were hot pressed.

TABLE XXIV: BENDING STRENGTH VB<sub>2</sub> (84)

Temperature (°C)	Strength (psi)
RT	20,800
600	22,000
800	21,800
1000	23,300
1100	40,500
1200	17,800
*1450	17,000

\*No bend. Very severe oxidation.

According to Binder VB<sub>2</sub> is one of the poorest hard metals for elevated temperature service, since its poor oxidation resistance leads to low strength. These figures do not reflect the true strength of the material, because an inert atmosphere was not used. There was no evidence of plastic deformation in these VB<sub>2</sub> specimens. Specimens were approximately 1.0" x 0.4" x 0.2", and were hot pressed. (84)

TABLE XIV: HOT DEFORMATION TEST OF  $TiB_2$  (84)

Temperature (°C)	Thickness, Cm		Remarks
	Start	Finish	
1690	.815	.785	Surface oxidized.
1790	.525	.485	Some cracking, especially at edges.
1860	.54	.45	Cracking, especially at edges, some surface oxidation.
1870	.52	.48	Hit near one edge.
1870	.48	.455	Cracked and broke.

Test Method: Specimens, generally 1.0" x 0.4" x 0.2", were heated in air with an oxy-acetylene torch, quickly slid into the cup of a small drop hammer, and hit with a single sharp stroke. A rough test, but indicative of whether materials could be hot deformed. Forming by hot pressing. One specimen of  $VB_2$  split apart upon heating.

TABLE XVI: COMPRESSIVE STRENGTH

Diboride	Form	Temp (°C)	Strength (psi)	Ultimate Kg/mm <sup>2</sup>	Reference
$TiB_2$	Self bonded, Hot pressed	Room	97,000		72,94 26
		20		135	
		1000		22.7	
		1200		25.8	
		1400		18.3	
$ZrB_2$		1600		11.0	26
		20		159	
		1000		30.6	
		1200		24.1	
		1400		24.4	
$CrB_2$		1600		47.1	26
		20		128	
		1000		86.8	
		1200		40.2	
		1400		58.1	
		1600		41.2	

Fracture: The types of fracture in diboride specimens during compressive tests as reported by Samsonov (26) were as follows: At low temperatures, brittle fracture occurred in the direction of the applied force; at higher temperatures, the specimens had a barrel-shaped appearance or formed two truncated cones, showing a certain degree of plasticity being developed.



An apparatus for subjecting up to ten (10) cubic centimeters of material to pressures of 15,000 atmospheres at temperatures as high as 10,000°C was developed during a study by Hall (81) of Brigham Young University. The purity or grain size of powders used was not provided, but selected facts from the report are reported for general interest.

1.  $ZrB_2$  Powder: Pressure about 9000 atmospheres, maximum temperature about 6500°C. A compressive test on a 1/8" diameter by 1/8" long specimen was run. Failure occurred at 300,000 psi.

2.  $TiB_2$  Powder: Pressure about 6000 atmospheres, maximum temperature about 7000°C. One piece .207" diameter by 3/8" long was subjected to compressive test. Failure occurred at 417,000 psi load.

3.  $TiB_2$  Powder: Pressure about 9000 atmospheres, maximum temperature about 7000°C. One piece .228" diameter by 3/8" long was subjected to compressive test. Failure occurred at 540,000 psi load.

TABLE XXVII: ELASTIC MODULUS (26)

Diboride	Elastic Modulus $E \cdot 10^3, \text{ Kg/mm}^2$
$TiB_2$	54.0
$ZrB_2$	35.0
$VB_2$	27.3
$TaB_2$	26.2
$CrB_2$	21.5

TABLE XXVIII: ELASTIC CONSTANTS OF  $TiB_2$  (95)

Direction	Elastic Constant
$C_{11}$	6.9
$C_{33}$	4.4
$C_{44}$	2.5
$C_{12}$	4.1

Crystals were grown by means of arc-fusion process by the Linde Company. The theoretical density was assumed in calculating the elastic constants. Four of the five constants were measured. The  $TiB_2$  crystal was 1/4" in diameter by 5/8" in length.

TABLE XXIX: DESIGN CHARACTERISTICS (89\*)

Material	Specific Stiffness $E/P, \text{ in } \times 10^6$	**Weight/Strength Ratio $P/\sqrt{E} \times 10^{-6}$	Specific Compressive Strength, $\sigma_c/P, \text{ in } \times 10^3$	Specific Tensile $\sigma_t/P, \text{ in } \times 10^3$
ZrB <sub>2</sub>	195	32	—	—
TiB <sub>2</sub>	—	—	350	—
CrB <sub>2</sub>	—	—	—	550
Mixed Boride	625	14	5800	—
Al <sub>2</sub> O <sub>3</sub>	395	19	2950	300
BN	160	22	—	200
B <sub>4</sub> C	720	10	4600	500

\*Approximate figures obtained from interpolation of bar charts.

\*\*For slender columns of stable cross section the proper weight/strength factor uses the  $\sqrt{E}$ , placing more value on density. The efficiency of the material increases as the figures decrease.

Abbreviations: E - Modulus of elasticity in psi.

P - Density in lb/in<sup>3</sup>.

$\sigma_c$  - Ultimate compressive stress in psi.

$\sigma_t$  - Ultimate tensile stress in psi.

# Chemical Properties:

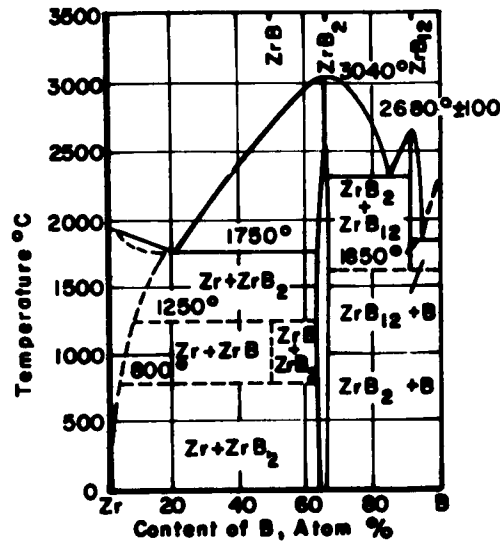


Figure 11. Zirconium-Boron Phase Diagram (Ref 26)

$ZrB_2$  appears as an intermediate congruent melting phase with a very narrow homogeneity region within the zirconium boron system. It is the highest melting compound in the system.

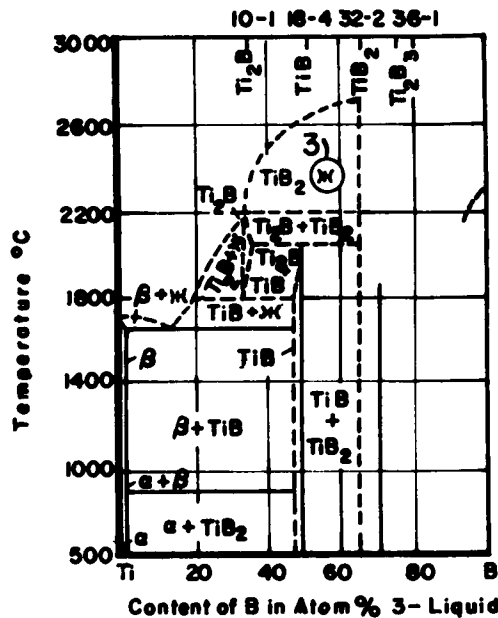


Figure 12. Titanium-Boron Phase Diagram (Ref 26)

The titanium-boron phase diagram has not been completed. The diagram shown above is the latest available in the open literature. It appears that  $TiB_2$  will form an intermediate congruent melting phase, having a homogeneity region of about 8 atom percent.

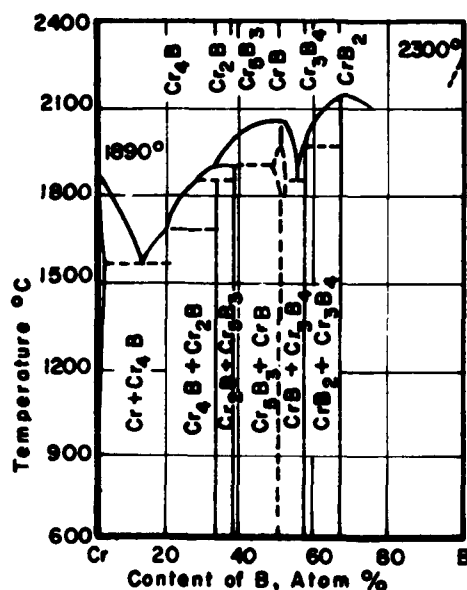


Figure 13. Chromium-Boron Phase Diagram (Ref 26)

CrB<sub>2</sub> has been established as one of the existing compounds in the chromium-boron system. Data, other than its stoichiometric composition and solid solution with Cr<sub>3</sub>B<sub>4</sub> is not provided on present diagrams. It is presently the highest melting compound in the system.

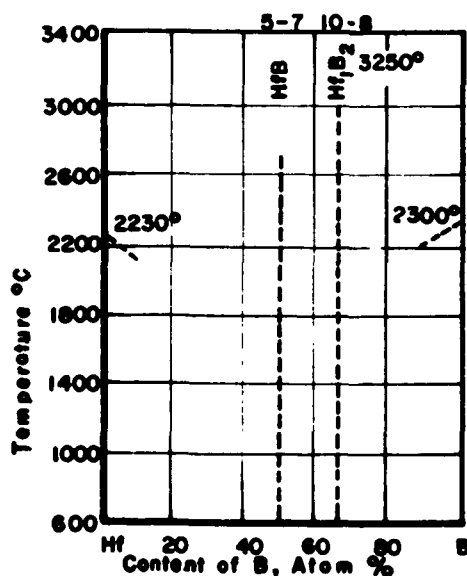


Figure 14. Hafnium-Boron Phase Diagram (Ref 26)

The diagram of the hafnium-boron system is not presently available in the open literature. A preliminary study is shown in the above figure, and shows that only the compound HfB<sub>2</sub> has been definitely established.

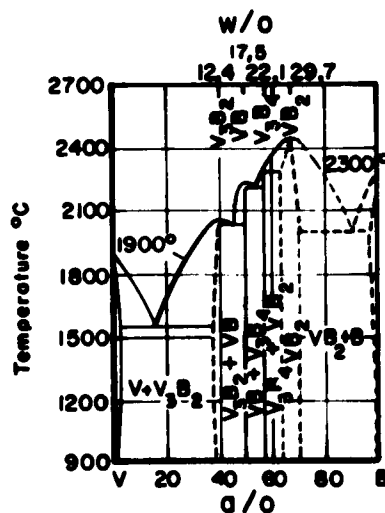


Figure 15. Vanadium-Boron Phase Diagram (Ref 90)

$\text{VB}_2$  is the highest melting phase ( $2400^\circ\text{C}$ ) in the vanadium-boron system. It is an intermediate congruent melting phase and has a narrow homogeneity region on either side of the stoichiometric composition.

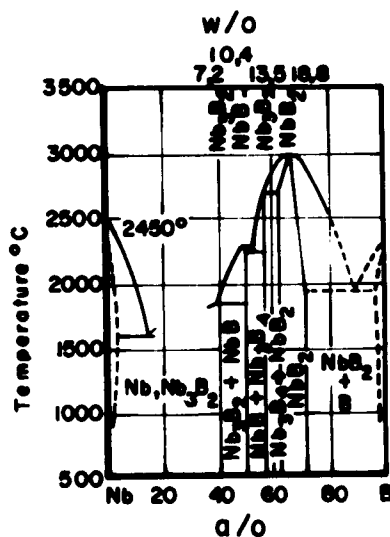


Figure 16. Niobium-Boron Phase Diagram (Ref 90)

$\text{NbB}_2$ , like  $\text{VB}_2$  and  $\text{TaB}_2$ , is an intermediate congruent melting phase and the highest melting point in the system. It has a wider homogeneity region than  $\text{VB}_2$ , which at low temperatures is about 10 atom percent.

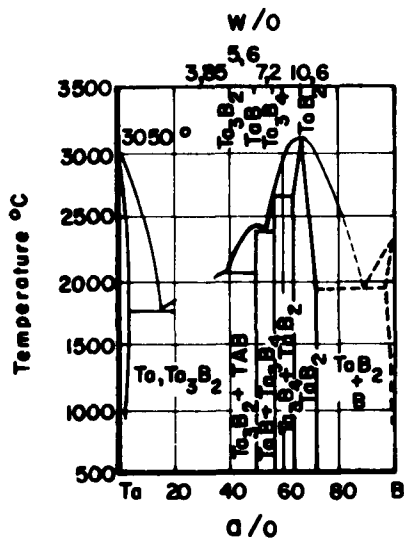


Figure 17. Tantalum-Boron Phase Diagram (Ref 90)

The tantalum-boron system is similar to the niobium-boron system. TaB<sub>2</sub> is the highest melting compound in the system and is an intermediate congruent melting phase. It also has a homogeneity region at low temperatures of about 10 atom percent.

The thorium-boron system has not been investigated to the extent of constructing a phase diagram. ThB<sub>4</sub> has been established as one of the existing compounds in the systems.

Diffusion (91): Technique used in determining the diffusion characteristics in the following tables are described below. (Taken directly from original article).

Specimens, 3 to 4 mm diameter cylinders, were charged with carbon by placing the specimens in a suitable holder and were surrounded with lamp black. For saturation with boron, a charge of 99.1 percent purified amorphous boron was used in a mixture of 3 percent  $\text{NH}_4\text{Cl}$  as a diffusion activator. The time at temperature for each temperature was two hours. On the basis of weight changes, hardness data, metallographic observations, and x-ray analyses, the compounds formed on the surface were determined.

Diffusion constants (which appear to really be constants associated with the rate of growth of the compound layer) were calculated from the relation

$$D (C - C_2) = C_0 K$$

where D is the diffusion coefficient,  $C - C_2$  is the difference in concentration of the metalloid on the boundaries of the layers, and K is defined as

$$K = \frac{1 - x^2}{4t} \ln x \cdot R^2$$

where x is the radius of the specimen (R) minus the thickness of the diffusion zone and t is the time.

The activation energy, Q, was calculated from the relation

$$D (C - C_2) = D_0 \exp (-Q/RT).$$

Interstitial Diffusion (91): Tantalum-Boron -  $D = 5.92 \times 10^3 \exp (-16,900 \pm 6,100)/RT$ . The growth of the  $\text{TaB}_2$  phase was used for determining the diffusion coefficient over the temperature range of 1200 to 2000°C. As previously mentioned the validity of these values as diffusion data is very questionable.

TABLE XXX: DIFFUSION IN TANTALUM-BORON SYSTEM

Temp (°C)	D (C - C <sub>2</sub> )	Q (cal/mole)	D <sub>0</sub> (cm <sup>2</sup> /sec)	C - C <sub>2</sub> (g/cm <sup>3</sup> )	D (cm <sup>2</sup> /sec)
1200	11.8206	16,900 $\pm$ 6100	1280 $\pm$ 240	0.216	$5.92 \times 10^3 \exp \frac{(-16,900)}{RT}$
1300	27.3438				
1400	44.1540				
1500	65.9340				
1600	86.3874				
1800	99.6530				
2000	125.5320				

Niobium-Boron -  $D = 4.74 \times 10^3 \exp \frac{-(14,300 \pm 5400)}{RT}$  over the temperature range of 1400 to 2000°C. The "diffusion coefficient" was determined from the measured rates of growth of the NbB<sub>2</sub> phase.

TABLE XXXI: DIFFUSION IN NIOBIUM-BORON SYSTEM

Temp (°C)	D (C - C <sub>2</sub> )	Q (cal/mole)	D <sub>0</sub> (cm <sup>2</sup> /sec)	C - C <sub>2</sub> (g/cm <sup>3</sup> )	(cm <sup>2</sup> /sec)
1400 1600 1800 2000	5.4550 9.5490 12.1980 14.0580	14,130 $\pm$ 4900	1420 $\pm$ 280	0.254	$5.62 \times 10^3 \exp \frac{-(14,130)}{RT}$

Titanium-Boron -  $D = 2.15 \times 10^4 \exp \frac{-(9,150 \pm 2,800)}{RT}$  over the temperature range of 800 to 1200°C. The "diffusion coefficient" was determined from the measured rates of growth of the TiB<sub>2</sub> phase.

TABLE XXXII: DIFFUSION IN TITANIUM-BORON SYSTEM

Temp (°C)	D (C - C <sub>2</sub> )	Q (cal/mole)	D <sub>0</sub> (cm <sup>2</sup> /sec)	C - C <sub>2</sub> (g/cm <sup>3</sup> )	(cm <sup>2</sup> /sec)
800 1000 1100 1200	54.7000 112.4350 150.0640 178.6530	9,150 $\pm$ 2,800	7880 $\pm$ 1230	0.333	$2.15 \times 10^4 \exp \frac{-(9,150)}{RT}$

TABLE XXXIII: CHEMICAL COMPOSITION CHANGE IN VACUUM  
AFTER HEATING TO 1700°C (78)

Diboride	Metal/Non-Metal Ratio		B/A
	Before Test (A)	After Test (B)	
TiB <sub>2</sub>	2.21	2.09	0.945
ZrB <sub>2</sub>	4.21	4.21	1.000
CrB <sub>2</sub>	2.40	2.59	1.080

Oxidation: In regards to oxidation resistance, the borides can be considered as a special group of high melting compounds. Unlike the carbides and nitrides, they are not decisively influenced by the formation of a pseudomorphic



layer (solid solution of the lowest oxide forming on the boundary between the compound and the oxide layer). The oxidation rate of diborides is determined by, the nature of the oxide film structure, and its protective properties. The two protective processes are evaporation of the boron anhydride and formation of borates. Because of these processes it is impossible to evaluate the oxidation resistance of borides by the weight curve ( $\text{g/cm}^2$ ) (26).

The protective function of the oxide layer may be approximated by the so-called Pilling-Bedvords ratio:  $\alpha = M.d/mD$ , where  $M$  is the molecular weight of the oxide resulting from oxidation of one gram-molecule of the compound,  $m$  is the molecular weight of the compound oxidized and  $D$  and  $d$  are the densities of the oxide and the compound, respectively. For  $\alpha < 1$  oxidation is continuous while for  $\alpha > 1$  there is variation in oxidation rate (26).

Pilling-Bedvords Ratio ( $\alpha$ ) for certain diboride compounds.

Diboride	( $\alpha$ )
TiB <sub>2</sub>	1.21
ZrB <sub>2</sub>	1.16
HfB <sub>2</sub>	1.71
TaB <sub>2</sub>	1.48

The data available in the literature on temperature of oxidation is confusing and dependent upon the author. Some interesting facts were selected and are given in the following paragraphs.

Campbell stated that VB<sub>2</sub> oxidized at 1100-1200°C, and HfB<sub>2</sub> in air forms an oxide film around 600-700°C. HfB<sub>2</sub> according to Samsonov disintegrates at 1000-1200°C (23).

Zirconium and titanium diborides have the best oxidation resistance, being resistant for extended periods of time at 1300°C (2370°F) and 1400°C (2550°F), respectively (1).

A zirconium boride hot pressed configuration being 1.25 inches long with a 0.375 radius at the end was tested for approximately 60 seconds in a Mach 2 airstream having a stagnation temperature of approximately 3800°F and stagnation pressure of 105 psig. The results of this test by NASA showed that the boride specimen remained intact (94).

TABLE XXXIV: CORROSION DEPTH IN OXIDATION OF CERTAIN DIBORIDES  
(Oxidation Temperature 1000°C) (26)

Diboride	Oxidation Time Hours	Depth of Corrosion (mm)
TiB <sub>2</sub>	0.8	0.10
TiB <sub>2</sub>	9.3	0.28
TiB <sub>2</sub>	19.	0.37

TABLE XXXIV: CORROSION DEPTH IN OXIDATION OF CERTAIN DIBORIDES (CONTINUED)  
(Oxidation Temperature 1000°C) (26)

Diboride	Oxidation Time Hours	Depth of Corrosion (mm)
TiB <sub>2</sub>	40.	0.52
TiB <sub>2</sub>	82.5	0.62
TiB <sub>2</sub>	102.	0.59
TiB <sub>2</sub>	147	0.58
TiB <sub>2</sub>	170	0.61
ZrB <sub>2</sub>	170	0.54
CrB <sub>2</sub>	40	0.38

TABLE XXXV: CHEMICAL-CORROSION RESISTANCE\*

Boride	General Comments	Reference
ZrB <sub>2</sub>	Stable in presence of carbon; slightly attacked by cold HCl, rapidly by HNO <sub>3</sub> , dissolves in aqua regia, reacts with hot H <sub>2</sub> SO <sub>4</sub> , attacked by fused alkali hydroxides, carbonates, and bisulfates. Reacts with brown lead oxide and sodium peroxide; weight gain in still air for 100 hours at 1000°C equals 6 mg/cm <sup>2</sup> , corrosion limit in liquid aluminum equals 800°C, behaves good in liquid steel.	8,22,27
TiB <sub>2</sub>	Stable in presence of carbon; not attacked by HCl or HF. Reacts with H <sub>2</sub> SO <sub>4</sub> , dissolves in HNO <sub>3</sub> -H <sub>2</sub> O; weight gain in still air for 100 hours at 1000°C equals 4-6 mg/cm <sup>2</sup> , corrosion limit in liquid aluminum equals 1500°C, behaves fair in liquid steel.	18,22,27
NbB <sub>2</sub>	Soluble in sulfuric or hydrofluoric acids, stable in presence of carbon, not attacked by HCl, HNO <sub>3</sub> , aqua regia, dissolves in alkali hydroxides, carbonates, bisulfates, and sodium peroxide.	8,22
TaB <sub>2</sub>	Soluble in sulfuric or hydrofluoric acid, stable in presence of carbon, not attacked by HCl, HNO <sub>3</sub> , aqua regia, dissolves in fused alkali hydroxides, carbonates, bisulfates, and peroxides.	8,22,27
ThB <sub>4</sub>	Soluble in nitric, hydrochloric acid, and hot sulfuric acid, unstable in presence of carbon.	8,27

TABLE XXXV: CHEMICAL-CORROSION RESISTANCE\* (CONTINUED)

Boride	General Comments	Reference
CrB <sub>2</sub>	Decomposes in streaming ammonia at 1100°C, stable in presence of carbon.	8,27,73
VB <sub>2</sub>	Stable in presence of carbon, insoluble in HCl, HF, H <sub>2</sub> SO <sub>4</sub> , soluble in HNO <sub>3</sub> , decomposes by melting alkali hydroxides, carbonates, nitrates, and bisulfates. Reacts violently with brown lead oxide and sodium peroxide.	8,27,75

\*Selected article number 3 of Appendix II provides detailed coverage on chemical resistance of certain boride compounds.

Additional observations as recorded by Samsonov, were selected by the author and are listed in the following paragraphs (26).

1. Chromium boride by hot pressing resists attack by fused salts and metals, including copper, tin, magnesium, silicon, and the fluorides.
2. Titanium, zirconium, and chromium borides formed from hot pressing technique show practically no reaction with fused tin, bismuth, lead or zinc.
3. Chromium and zirconium borides show low wettability by molten iron.
4. Copper fused in argon at 1100-1500°C in vacuum does not wet TiB<sub>2</sub>. Nickel fused in a helium atmosphere starts to wet TiB<sub>2</sub> after about 20 minutes.
5. Nickel corrodes the surface of NbB<sub>2</sub> in helium without fusion at 1550°C.
6. Molten copper does not wet VB<sub>2</sub> at 1100-1400°C in argon, but does wet ZrB<sub>2</sub> and TaB<sub>2</sub>.
7. The surface of TaB<sub>2</sub> is not wetted by fused silver in an argon atmosphere at 1300°C.
8. The diborides are not wetted by copper in the same degree, but increases in the following series: TiB<sub>2</sub>, VB<sub>2</sub>, NbB<sub>2</sub>, ZrB<sub>2</sub>, TaB<sub>2</sub>, CrB<sub>2</sub>.
9. Zirconium diboride at 1550°C in vacuum is corroded by iron, nickel and cobalt.
10. Hot pressed formed crucibles of TiB<sub>2</sub>, CrB<sub>2</sub>, and ZrB<sub>2</sub> prepared by Norton Company showed appreciable solubility in molten titanium (92).

The following tables on interactions involving diboride, includes many interesting observations.

TABLE XXVI: REFRACTORY PROPERTIES (26)  
(Nature of Interaction Between Boride Refractories and Fused Metals)

Atmosphere	Melt	Temp (°C)	Holding Time Hours	Content of Crucible Metal in Fused Metal (%)	Nature of Interaction
		Crucible Material TiB <sub>2</sub>			
Air	Tin	350	10	Traces of Ti	Ingot easily pulled from crucible
Air	Tin	350	40	Traces of Ti	Same
Air	Bismuth	375	10	Traces of Ti	Same
Air	Bismuth	375	40	Ti 0.05	Same
Air	Lead	450	10	Traces of Ti	Same
Air	Lead	450	40	Ti 0.06	Same
Air	Cadmium	450	10	Traces of Ti	Same
Air	Cadmium	450	40	Ti 0.026	Same
CO / N <sub>2</sub>	Steel	1600	5 min	—	Reacts with crucible which breaks up
CO / N <sub>2</sub>	Iron	1600	5 min	—	Same
Argon	Aluminum	1040	30 min	—	No reaction
Argon	Silicon	1600	10 min	—	Slight wetting, no noticeable reaction
Argon	Chromium	1860	10 min	—	Interaction with formation of eutec- tic alloys and new phases
Argon	Nickel	1600	5 min	—	Active reaction
CO / N <sub>2</sub>	Cobalt	1600	5 min	—	No noticeable reaction
Same	Welding slag based on CaF <sub>2</sub> *	1500	20 min	—	Same

\*Chemical composition of slag: 97.48 CaF<sub>2</sub>, 1.28 SiO<sub>2</sub>, 1.12 CaO, 0.075 S, 0.045 P.

TABLE XXVI: REFRACTORY PROPERTIES (26) (CONTINUED)  
(Nature of Interaction Between Boride Refractories and Fused Metals)

Atmosphere	Melt	Temp (°C)	Holding Time Hours	Content of Crucible Metal in Fused Metal (%)	Nature of Interaction
Crucible Material TiB <sub>2</sub>					
CO / N <sub>2</sub>	Welding slag based on SiO <sub>2</sub> **	1350	20 min	—	No noticeable reaction
Argon	Aluminum	1150	15 min	—	Does not react
Argon	Silicon	1600	3 min	—	Same
Argon	Chromium	1860	10 min	—	Reacts with forma- tion of new phases
Argon	Nickel	1600	5 min	—	Same
Argon	Cobalt	1710	5 min	—	Reacts with forma- tion of new phases
CO / N <sub>2</sub>	Welding slag based on CaF <sub>2</sub> *	1500	20 min	—	No reaction
Same	Welding slag based on SiO <sub>2</sub> **	1350	20 min	—	Same
Same	Steel	1600	2	—	Same
Air	Brass	850	86	—	Same
Crucible Material CrB <sub>2</sub>					
Air	Tin	350	10	Traces of Cr	Ingot easily pulled from crucible
Air	Tin	350	40	Cr 0.01	Same
Air	Bismuth	375	10	Traces of Cr	Same
Air	Bismuth	375	40	Cr 0.01	Same

\* Chemical composition of slag: 97.48 CaF<sub>2</sub>, 1.28 SiO<sub>2</sub>, 1.12 CaO, 0.075 S, 0.045 P.

\*\* Chemical composition of slag: 43.28 SiO<sub>2</sub>, 1.2 Al<sub>2</sub>O<sub>3</sub>, 1.0 FeO, 5.25 CaO, 5.28 MgO, 40.48 MnO, 3.6 CaF<sub>2</sub>, less than 1.15% P.

TABLE XXIV: REFRACTORY PROPERTIES (26) (CONTINUED)  
(Nature of Interaction Between Boride Refractories and Fused Metals)

Atmosphere	Melt	Temp (°C)	Holding Time Hours	Content of Crucible Metal in Fused Metal (%)	Nature of Interaction
		Crucible Material CrB <sub>2</sub>			
Air	Lead	450	10	Traces of Cr	Same
Air	Lead	450	40	Cr 0.01	Same
Air	Cadmium	450	10	Traces of Cr	Same
Air	Cadmium	450	40	Traces of Cr	Same
CO / N <sub>2</sub>	Steel KhVG	1620	5 min	—	Reacts with crucible which breaks up
Same	Carbon Steel	1620	5 min	—	Ingot wets crucible walls slightly and can be pulled from it
Same	Iron	1520	5 min	—	Ingot easily extracted
Same	Basic slag	1520	5 min	—	Wetting
Same	Acid slag	1520	5 min	—	Wetting
Argon	Aluminum	1150	5 min	—	No reaction
Argon	Silicon	1600	5 min	—	Active reaction
CO / N <sub>2</sub>	Cobalt	1600	5 min	—	Reaction with welding to crucible walls
CO / N <sub>2</sub>	Welding slag based on CaF <sub>2</sub> *	1500	20 min	—	No reaction
CO / N <sub>2</sub>	Welding slag based on SiO <sub>2</sub> **	1350	20 min	—	Same

\* Chemical composition of slag: 97.48 CaF<sub>2</sub>, 1.28 SiO<sub>2</sub>, 1.12 CaO, 0.075 S, 0.045 P.

\*\* Chemical composition of slag: 43.28 SiO<sub>2</sub>, 1.2 Al<sub>2</sub>O<sub>3</sub>, 1.0 FeO, 5.25 CaO, 5.28 MgO, 40.48 MnO, 3.6 CaF<sub>2</sub>, less than 1.15% P.

TABLE XXXVII: STABILITY IN ACIDS\* (26)

Diboride	Acid	Sp. Gr.	Weight Loss (in % of initial weight) Over Period of		
			1 Day	4 Days	10 Days
TiB <sub>2</sub>	HCl	1.19	0.1	0.4	0.8
	HNO <sub>3</sub>	1.42	6.1	15.1	30.5
	H <sub>2</sub> SO <sub>4</sub>	1.84	0.1	0.4	1.0
ZrB <sub>2</sub>	HCl	1.19	2.5	4.9	10.4
	HNO <sub>3</sub>	1.42	5.6	13.6	33.3
	H <sub>2</sub> SO <sub>4</sub>	1.84	1.2	4.2	5.2

\*Cold solutions, hot pressed specimens.

TABLE XXXVIII: SOLUBILITY IN NaOH SOLUTIONS (26)  
(Room temperature during 24 hours, boiling for 2 hours\*)

Diboride		NaOH(30% solution)	NaOH(10% solution)
TiB <sub>2</sub>	Cold	92	—
	Boiling	***	***
ZrB <sub>2</sub>	Cold	***	—
	Boiling	—	**
VB <sub>2</sub>	Cold	64	—
	Boiling	61	56
NbB <sub>2</sub>	Cold	95	—
	Boiling	—	95
TaB <sub>2</sub>	Cold	***	—
	Boiling	**	45
CrB <sub>2</sub>	Cold	99	—
	Boiling	88	98

\* Diboride powders produced by thermal-vacuum method were used for the investigation; pure compounds.

\*\* Decomposition of most of diboride with salt residue formation.

\*\*\*Partial hydrolysis.

**TABLE XXXIX: SOLUBILITY IN ACIDS (26)**  
(24 hours at room temperature and 2 hours at boiling)

	Acid		TiB <sub>2</sub>	ZrB <sub>2</sub>	VB <sub>2</sub>	NbB <sub>2</sub>	TaB <sub>2</sub>	CrB <sub>2</sub>
HCl	Concentrated Sp. Gr. 1.19	Cold	94	91	63	98	100	36
		Boiling	58	6	3	91	99	3
"	Dilute (1:1)	Cold	95	93	62	99	100	51
		Boiling	61	7	10	95	98	5
HNO <sub>3</sub>	Concentrated Sp. Gr. 1.4	Cold	28	12	1	94	100	99
		Boiling	*	*	2	100	100	22
"	Dilute (1:1)	Cold	31	23	3	99	100	99
		Boiling	*	4	2	100	100	41
H <sub>2</sub> SO <sub>4</sub>	Concentrated Sp. Gr. 1.84	Cold	89	65	49	100	99	99
		Boiling	58	1	13	3	3	—
"	Dilute (1:1)	Cold	96	51	60	100	100	9
		Boiling	68	5	7	92	99	3
H <sub>3</sub> PO <sub>4</sub>	Concentrated	Cold	98****	63**	66**	100***	100***	100***
		Boiling	—	—	—	—	—	—
"	Dilute (1:4)	Cold	98	89***	62	100	100	100
		Boiling	65	—	24	94	100	18
HClO <sub>4</sub>	Concentrated	Cold	30	10	4	—	100	96
		Boiling	**	4	0	—	100	0
"	Dilute	Cold	87	71	47	98	100	100
		Boiling	28	48	2	88	99	4
H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	Saturated	Cold	94	55	60	97	100	44
		Boiling	51	5	17	50	94	2
"	Dilute	Cold	89***	38***	58	93	99	97
		Boiling	—	—	37	98	99	75
HF	Concentrated	Boiling	64	25	13	44	20	2

\* Complete solution with formation of hydrolytic residue.

\*\* Rapid decomposition of diboride with formation of salt residue.

\*\*\* Decomposition of most of diboride with formation of salt residue.

\*\*\*\*Partial hydrolysis.



TABLE XXXX: SOLUBILITY OF MIXED ACIDS (26)  
(24 Hours at Room Temperature, 2 Hours' Boiling)

	Acid		Undissolved Part of Residue in %				
			TiB <sub>2</sub>	ZrB <sub>2</sub>	NbB <sub>2</sub>	TaB <sub>2</sub>	CrB <sub>2</sub>
Aquaregia	Concentrated (3 parts of HCl of sp. gr. 1.19 / 1 part HNO <sub>3</sub> of sp. gr. 1.43)	Cold	9***	7	71	99/	80
		Boiling	—	6	80	*	29
	Dilute: 3 parts HCl (1:1), 1 part HNO <sub>3</sub> (1:1)	Cold	3***	15	96	99	95
		Boiling	—	6	/	*	27
Oxalic Acid	30 ml of saturated solution / 10 ml of 30% H <sub>2</sub> O <sub>2</sub> / 10 ml of HNO <sub>3</sub> of sp. gr. 1.43	Cold	1	6	5	32	99
		Boiling	6	6	26	*	89
	30 ml of saturated solution / 20 ml of H <sub>2</sub> SO <sub>4</sub> of sp. gr. 1.84	Cold	87	59	92	99	31
		Boiling	50	10	86	99	3
HCl	35 ml at sp. gr. 1.19 / 15 ml bromine water	Boiling	35	18	58	99	2
HClO	35 ml concentrated / 15 ml concentrated HCl of sp. gr. water	Cold	27	90	73	99	48
		Boiling	***	8	60	100	3
	1 part at sp. gr. 1.84 / 4 parts of concentrated H <sub>3</sub> PO <sub>4</sub> / 2 parts of H <sub>2</sub> O	Cold	91	***	**	***	86
		Boiling	48	***	10	23	6
H <sub>2</sub> SO <sub>4</sub>	50 ml at sp. gr. 1.84 / 5 g	Boiling	6	6	3	5	/
	35 ml at sp. gr. 1.84 / 35 ml of HNO <sub>3</sub> of sp. gr. 1.43	Boiling	—	7	—	6	/
HNO <sub>3</sub>	sp. gr. 1.43 / HF (1 hour of heating)		1	4**	***	/	2
		Boiling	1**	4**	32	4	

\* Partial hydrolysis.

\*\* Very rapid solution (15 minutes).

\*\*\*Decomposition of most of boride with formation of residue.

Thermo-Physical Properties:

TABLE XXXXI: EVAPORATION BEHAVIOR AND VAPOR PRESSURE (26)

Diboride	Vapor Pressure mm Hg	Rate of Evaporation g/cm <sup>2</sup> sec	Temperature (°C)
TiB <sub>2</sub>	3.51 x 10 <sup>-6</sup>	0.427 x 10 <sup>-7</sup>	1200
	8.87 x 10 <sup>-6</sup>	1.08 x 10 <sup>-7</sup>	1400
	1.16 x 10 <sup>-5</sup>	1.33 x 10 <sup>-7</sup>	1600
	1.97 x 10 <sup>-5</sup>	2.16 x 10 <sup>-7</sup>	1800
ZrB <sub>2</sub>	0.96 x 10 <sup>-6</sup>	0.15 x 10 <sup>-7</sup>	1400
	7.2 x 10 <sup>-6</sup>	1.03 x 10 <sup>-7</sup>	1600
	3.22 x 10 <sup>-5</sup>	3.84 x 10 <sup>-7</sup>	1800
CrB <sub>2</sub>	1.71 x 10 <sup>-5</sup>	2.89 x 10 <sup>-7</sup>	1200
	3.82 x 10 <sup>-5</sup>	4.76 x 10 <sup>-7</sup>	1400
	6.64 x 10 <sup>-5</sup>	7.68 x 10 <sup>-7</sup>	1600
	1.2 x 10 <sup>-3</sup>	1.3 x 10 <sup>-5</sup>	2000

TABLE XXXXII: EVAPORATION-VAPOR-PRESSURE IN A VACUUM (78)

Diboride	Vapor Pressure (p x 10 <sup>5</sup> mm Hg)	*Rate of Evaporation g/cm <sup>2</sup> sec	Temperature (°C)
TiB <sub>2</sub>	0.350	0.427	1300
	0.890	1.080	1400
	0.545	0.63	1500
	1.162	1.330	1600
	1.985	2.185	1700
ZrB <sub>2</sub>	1.967	2.165	1800
	0.100	0.150	1400
	0.834	1.248	1500
	0.720	1.030	1600
	1.417	1.969	1700
CrB <sub>2</sub>	3.227	3.843	1800
	1.710	2.890	1200
	3.560	4.520	1300
	3.820	4.760	1400
	1.200	1.450	1500
	6.640	7.680	1600
	4.620	4.980	1800

\*Measure by Langmuir method. Laboratory vacuum furnace.

James Leitnaker of the Los Alamos Scientific Laboratory has made a recent thorough study on evaporation behavior of zirconium diboride. This study consisted of measuring vapor pressures of zirconium over zirconium diboride in a tungsten crucible over the temperature range 3420°F to 4000°F. Reaction of the solid boride with residual gases in the system producing volatile oxides was studied and measured pressures were corrected for the increased volatility. Different orifice sizes were used and the data therefrom used to obtain an evaporation coefficient of  $0.025 \pm 0.010$ . According to Leitnaker  $ZrB_2$  vaporizes to the equation  $ZrB_{1.906}(s) \rightleftharpoons Zr(g) + 1.906B(g)$  having an enthalpy of  $458.3 \pm 6.5$  Kcal/mole and an associated entropy change of  $98.4 \pm 3.0$  eu. The difference between the observed enthalpy and the calculated enthalpy (477.4 Kcal/mole) was explained on the basis of inconsistencies in the heat of vaporization of metallic zirconium (28).

TABLE XXXXIII: HEATS OF FORMATION\*

Diboride	Heats of Formation Kcal/mole	Remarks	Reference
TiB <sub>2</sub>	32**	$\Delta H_{298}^\circ$	88
	70.04	$\Delta H_{298}^\circ$ , standard heat	****26,34
	~ 72	of formation at 298°K	77
	73	Temperature range 298 -	96
	- 70	3253°K	87
ZrB <sub>2</sub>	63.1		***26,34
	> -78	$H_{298}^\circ$	77
NbB <sub>2</sub>	65		96
	> 36.	$H_{298}^\circ$	26,34,77
VB <sub>2</sub>	59		96
	62		96
TaB <sub>2</sub>	> 52	$H_{298}^\circ$	26,34,77
	63		96
CrB <sub>2</sub>	30	$H_{298}^\circ$	26,34,77
	19		34
	47		95

\* These values were obtained by calculations and were determined as a result of tensimetical experiments and the study of the products of the interaction of borides with nitrogen and carbon. Samsonov (34) showed that the heats of formation of compounds similar to metal (borides, etc.) are determined by the distribution of the electron configuration in their crystal lattices.

\*\* This heat is a factor of two less than that reported by Brewer and Samsonov. A mass spectrometer was used with a high temperature Kundsen cell.

\*\*\*A copy of the translated article by Samsonov (34) is provided in Appendix II. Abstracts 11 and 12 of Appendix I are provided for further information on heats of formation.

\*\*\*\*Nonporous bodies.

TABLE XXXIV: ENTROPY (26)

Diboride	Entropy cal/mole-degree
TiB <sub>2</sub>	7.52
ZrB <sub>2</sub>	10.7
HfB <sub>2</sub>	14.2
VB <sub>2</sub>	7.9
NbB <sub>2</sub>	10.4
TaB <sub>2</sub>	13.9
CrB <sub>2</sub>	9.4

Nonporous specimens.

TABLE XXXIV: THERMIONIC EMISSION (26)

Diboride	Work Function in Thermionic Emission $\phi$ , ev.
TiB <sub>2</sub>	3.88 ev.
ZrB <sub>2</sub>	3.67 ev.
VB <sub>2</sub>	3.95 ev.
NbB <sub>2</sub>	3.65 ev.
TaB <sub>2</sub>	2.89 ev.
CrB <sub>2</sub>	3.36 ev.

TABLE XXXVI: SPECIFIC HEAT OF TiB<sub>2</sub> (85)

Sym	Investigator	Material Composition	Test Method	Remarks
○	Walker, B.E. Ewing, C.F. Miller, R.R.	99.7% TiB <sub>2</sub> ; 0.2% B; 0.1% Fe	Drop method, copper calorimeter	Avg. scatter of heat content data $\pm$ 1%

"The mean specific heat of CrB<sub>2</sub> (70% Cr, 29.9% B, 0.05% C, 0.40% Fe) was determined on a water calorimeter set for the temperature range from room temperature to 300, 400, 500, 600, 700, and 800°C. On the basis of the data obtained the following equation for the relationship of specific heat to temperature was developed by the method of least squared:  $c = 0.1342 \times 10^{-4} T$ . An equation for the true specific heat capacity,  $c = 0.1061 \times 10^{-4} T$ , was also obtained" (86).

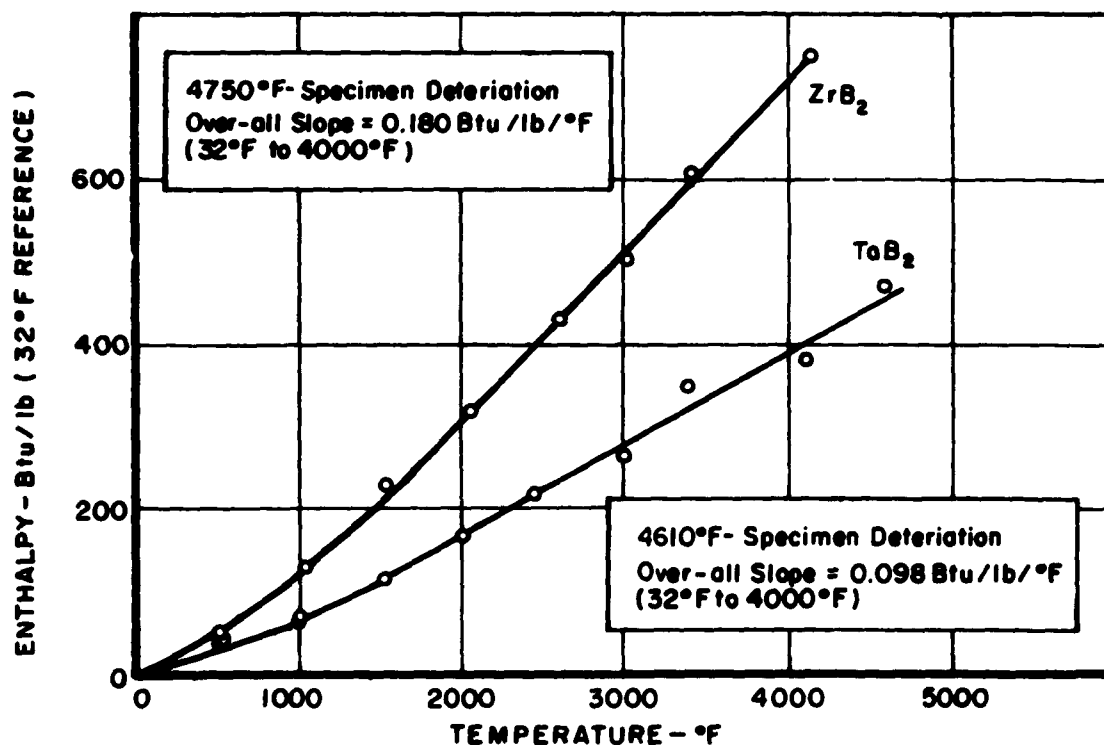
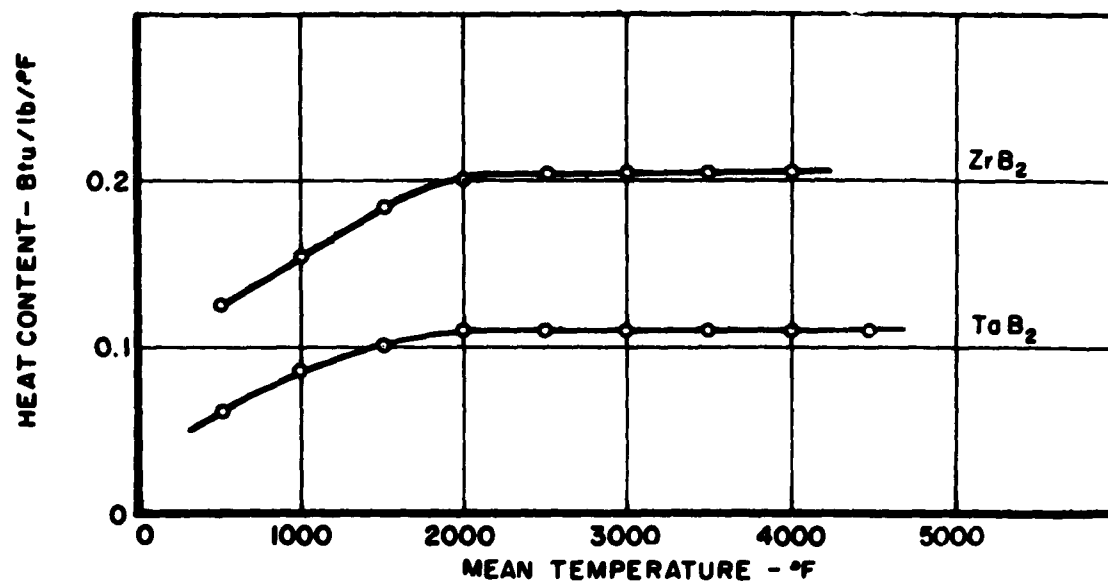
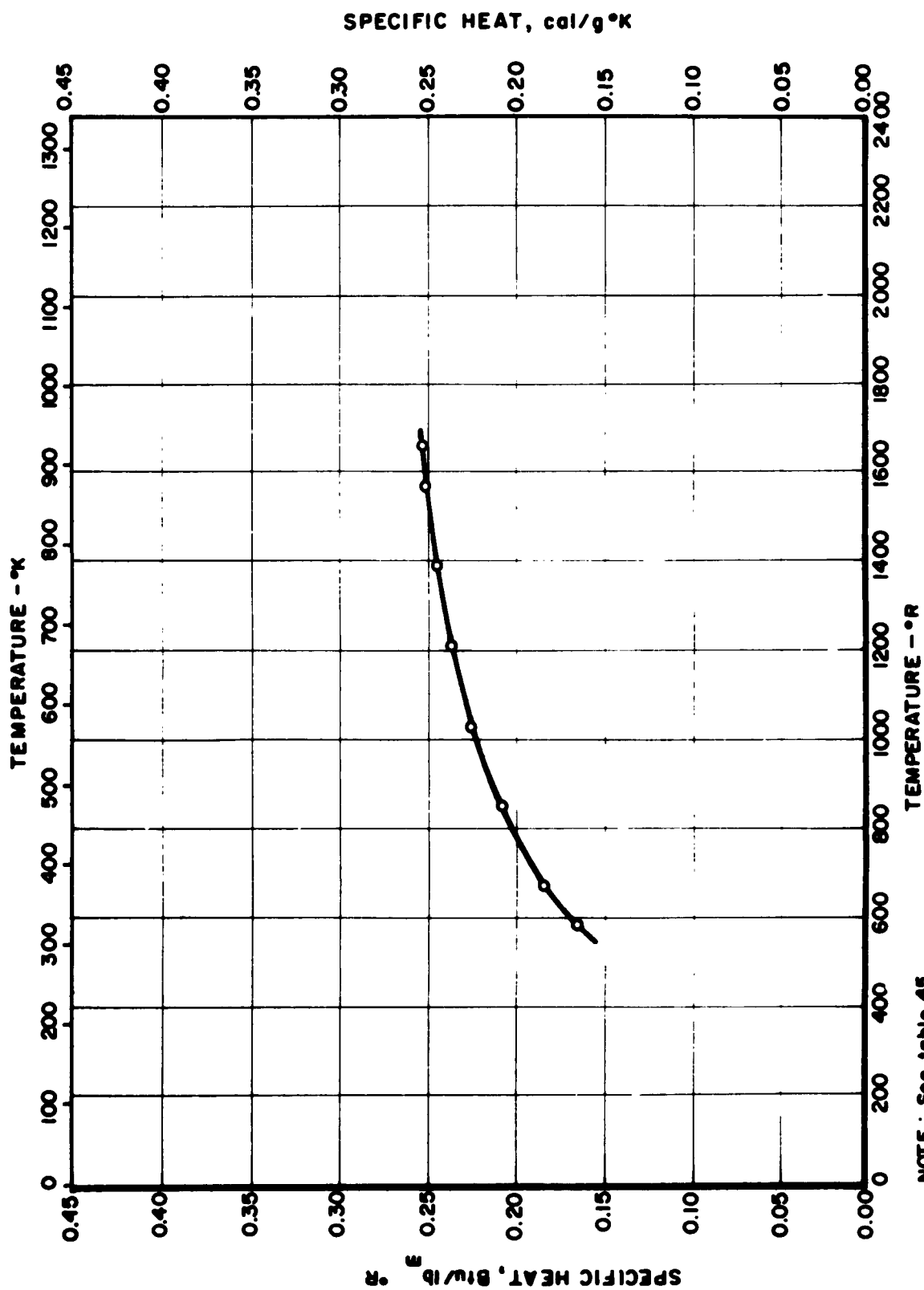


Figure 18. Enthalpy and Heat Content for  $ZrB_2$  and  $TaB_2$  (Ref 83)

Specimen supplied by Norton Company, hot pressed, 70-75% of theoretical density, density equals 4.14 g/cm<sup>3</sup> 3/4" diameter x approximately 3" length. Test Method: drop technique - ice calorimeter.



NOTE : See table 45

Figure 19. Specific Heat of TiB<sub>2</sub> (Ref 85)

TABLE XXXVII: STOICHIOMETRIC CHARACTERISTICS AND SPECIFIC GRAVITY (26)

Diboride	Stoichiometric Characteristics			Specific Gravity
	Molecular Wt.	Content of Nonmetal % by Wt.	Region of Homogeneity atom %	
TiB <sub>2</sub>	69.54	31.1	67-75	4.45
ZrB <sub>2</sub>	112.86	19.18	—	5.8
HfB <sub>2</sub>	200.2	10.8	—	10.5
VB <sub>2</sub>	72.59	29.8	—	4.6
NbB <sub>2</sub>	114.55	18.9	—	6.0
TaB <sub>2</sub>	202.52	10.7	—	11.7
CrB <sub>2</sub>	73.65	29.4	—	5.6

Total emissivities of NbB<sub>2</sub> were computed by General Electric Company (82) and recorded as follows:

Temperature		Total Emissivity of NbB <sub>2</sub>
1540°K	2322°F	.29
1800°K	2790°F	.32
2000°K	3150°F	.35

Abstract 13 of Appendix I is concerned with the emissivity of ZrB<sub>2</sub> and HfB<sub>2</sub>.

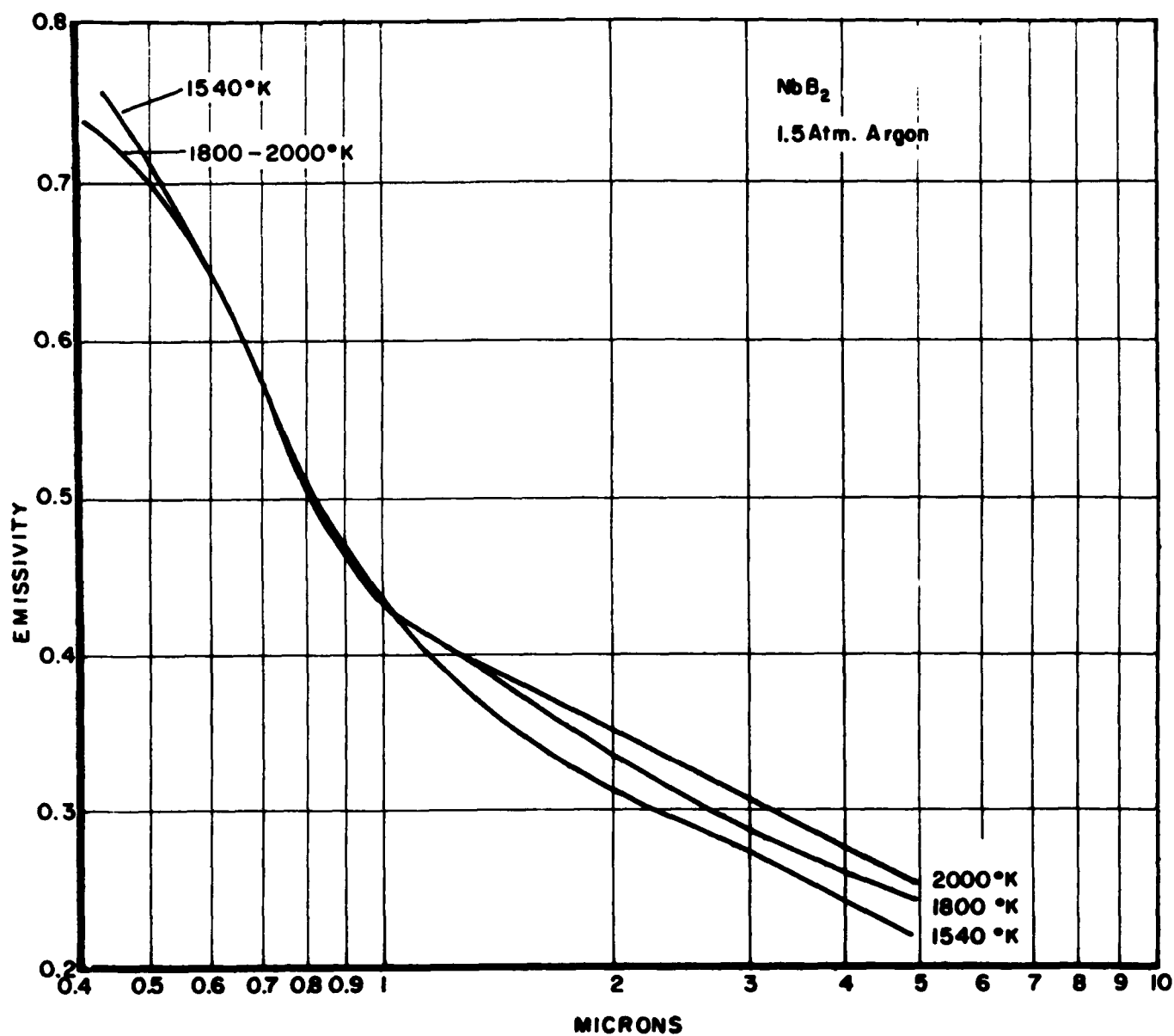


Figure 20. Spectral Emissivity of NbB<sub>2</sub> from 0.4-5.0 Microns and at 1540°K, 1800°K, 2000°K (Ref 82)  
 The NbB<sub>2</sub> specimen was manufactured by Carborundum Co., Latrobe, Pennsylvania. Purity not given, but stated as being of high purity. Test was run in 1.5 atmospheres of purified argon.



**Electrical Properties:**

**TABLE XXXVIII: ELECTRICAL RESISTIVITIES\***

Diboride	Temperature (°C)	Resistivity Microhm. cm	Temperature Coefficient of Resistivity $\rho \cdot 10^3$	Reference
TiB <sub>2</sub>	Room	15.2-28.4	2.78	22,70
	Room	11.4		26
	Room	15		43
ZrB <sub>2</sub>	Room	9-15	1.76	27,68
	1600	87.6		70
	1825	102.2		70
	2185	113.5		70
	2305	118.2		70
	2445	132.7		70
	2635	139.1		70
	Room	9-11		22,43
	Room	16.6		26
	Room	7-10		27,68
VB <sub>2</sub>	Room	16	3.16	22,43,70
	Room	19		26
	Room	16-38		27,68
NbB <sub>2</sub>	Room	28.4-65.5 ( $x=0.12\%$ )	1.39	70
	Room	32		22,43
	Room	34		26
TaB <sub>2</sub>	Room	12-65	1.48	27,68
	Room	68.-86.5 ( $x=0.085\%$ )		70
	Room	68		22,43
CrB <sub>2</sub>	Room	37.4	3.1	26
	Room	14-68		27,68
	Room	21		22,43,70
	Room	56		26
HfB <sub>2</sub>	Room	21-56	3.6	27,68
	Room	10 8.8		22,43 26

\*Varying porosity-average figures.

TABLE XXXIX: HALL COEFFICIENT - THERMO-EMF (79)

Diboride	Hall Constant	Thermo-Emf V/deg.
TiB <sub>2</sub>	-17.8	-5.1
CrB <sub>2</sub>	-1.1	-6.8
NbB <sub>2</sub>	-2.1	-1.4
HfB <sub>2</sub>	-17.	—
VB <sub>2</sub>	-1.1	—
ZrB <sub>2</sub>	-17.6	1.2
TaB <sub>2</sub>	-2.2	-3.1

NOTE: See abstract 14, Appendix I.

TABLE XXXX: SUPERCONDUCTIVITY (26)

Diboride	Temperature of Transition into Superconductive State °K
TiB <sub>2</sub>	< 1.26
ZrB <sub>2</sub>	< 1.8
HfB <sub>2</sub>	< 1.26
VB <sub>2</sub>	< 1.9
NbB <sub>2</sub>	< 1.27
TaB <sub>2</sub>	< 1.3

TABLE XXXXI: WIEDEMANN-FRANZ RATIOS (71)

Diboride	W-F Ratio
TiB <sub>2</sub>	$165 \times 10^{-8}$
ZrB <sub>2</sub>	$154-213 \times 10^{-8}$
NbB <sub>2</sub>	$179-262 \times 10^{-8}$
TaB <sub>2</sub>	$225 \times 10^{-8}$

# Nuclear Properties:

TABLE XXXXII: RADIATION (26)

Diboride	Temperature Range (°C)	Radiation Coefficient**
HfB <sub>2</sub> *	800-1700	0.88-0.93
ZrB <sub>2</sub>	800-1700	0.89-0.92
TiB <sub>2</sub>	800-1700	0.71
VB <sub>2</sub>	800-1700	0.72-0.76
CrB <sub>2</sub>	800-1700	0.72

\* Relatively high coefficient.

\*\*Interpolated from graph. Increases linear with temperature. The technique used for measurement of the radiation coefficients is described in "Optics and Spectroscopy" (Optika i Spektroskopiya), 1960, 8, 410, by Serebryakova, T. I., Paderno, Yu. B. and Samsonov, G. V.

Compatibility with Metallic Matrix (93): The data on the following tables was obtained from boride compounds having the following characteristics:

1. Powder size averaged 2-4 microns.
2. Cold pressed compacts were fixed at 40 volume percent dispersed boride and 60 volume percent metallic matrix.
3. Density was generally 75-85 percent of the calculated theoretical density.
4. Vacuum (<.1 u) was employed during the thermal treatment.
5. X-ray diffraction was used as the means of identifying the phases.

TABLE XXXXIII. COMPATIBILITY OF BORIDE WITH TITANIUM MATRIX, 1000°C, 2 HOURS

Dispersant	Phases Identified		Others
	Ti		
	a <sub>o</sub>	c <sub>o</sub>	
HfB <sub>2</sub>	2.97	4.76	HfF <sub>2</sub> (v.s.); TiB (v.w.)
TiB <sub>2</sub>	2.95	4.71	TiB <sub>2</sub> (v.s.); TiB (w.)
VB <sub>2</sub>	2.96	4.74	VB <sub>2</sub> (s.); TiB (w.); VB (t.)
ZrB <sub>2</sub>	2.96	4.78	ZrB <sub>2</sub> (v.s.); TiB (w.)

Code: v.w. - very weak pattern  
w. - weak pattern  
s. - strong pattern  
v.s. - very strong pattern  
t. - trace  
m. - medium pattern

TABLE XXXXIV. COMPATIBILITY OF BORIDE WITH ZIRCONIUM MATRIX, 1000°C, 2 HOURS

Dispersant	Phases Identified		Others
	Zr		
	a <sub>o</sub>	c <sub>o</sub>	
HfB <sub>2</sub>	3.25	5.16	HfB <sub>2</sub> (v.s.); ZrB (w.); ZrB <sub>2</sub> (w.)
TiB <sub>2</sub>	3.22	5.12	TiB <sub>2</sub> (s.); ZrB (w.); ZrB <sub>2</sub> (s.)
VB <sub>2</sub>	3.24	5.16	VB <sub>2</sub> (w.); ZrB (s.); ZrB <sub>2</sub> (s.)
ZrB <sub>2</sub>			ZrB <sub>2</sub> (v.s.); ZrB (v.w.)

TABLE XXXXV. COMPATIBILITY OF BORIDE WITH 304 STAINLESS STEEL MATRIX, 1000°C, 2 HOURS

Dispersant	Phases Identified
HfB <sub>2</sub>	HfB <sub>2</sub> (v.s.); Fe (s.); Fe <sub>2</sub> B (t.)
TiB <sub>2</sub>	TiB <sub>2</sub> (s.); Fe (s.); Fe <sub>2</sub> B (t.)
VB <sub>2</sub>	VB <sub>2</sub> (w.); VB (w.); Fe (s.); Fe (s.); Fe <sub>2</sub> B (w.)
ZrB <sub>2</sub>	ZrB <sub>2</sub> (v.s.); Fe (s.); Fe <sub>2</sub> B (v.w.)

TABLE XXXXVI. COMPATIBILITY OF BORIDE WITH IRON MATRIX, 1000°C, 2 HOURS

Dispersant	Phases Identified
HfB <sub>2</sub>	HfB <sub>2</sub> (v.s.); Fe (v.s.); Fe <sub>2</sub> B (w.)
TiB <sub>2</sub>	TiB <sub>2</sub> (v.s.); Fe (s.); Fe <sub>2</sub> B (v.w.)
VB <sub>2</sub>	VB <sub>2</sub> (v.w.); Fe <sub>2</sub> B (s.)
ZrB <sub>2</sub>	ZrB <sub>2</sub> (v.s.); Fe (s.); Fe <sub>2</sub> B (w.)

TABLE XXXXVII. COMPATIBILITY OF BORIDE WITH NICKEL BASE, 1000°C, 2 HOURS

Dispersant	Phases Identified
HfB <sub>2</sub>	HfB <sub>2</sub> (v.s.); Ni (v.s.); Ni <sub>2</sub> B (m.); Hf-Ni-B (s.)
TiB <sub>2</sub>	TiB <sub>2</sub> (s.); Ni (v.s.); Ti-Ni-B (s.)
VB <sub>2</sub>	VB <sub>2</sub> (m.); Ni (v.s.); Ni <sub>2</sub> B (s.); Ni <sub>1-x</sub> B <sub>y</sub> (s.)
ZrB <sub>2</sub>	ZrB <sub>2</sub> (v.w.); Ni (v.s.); Zr-Ni-B (s.)

TABLE XXXXVIII: COMPATIBILITY OF  $UO_2$  WITH BORIDES (80)

Boride	Melting and/or Reaction Temperature (°F)	Pressure (mm)		Remarks
		Initial	Final	
		Argon or Vacuum		
ZrB <sub>2</sub>	4700	40	72	Strong adherence; UO, UO <sub>2</sub> , ZrB <sub>2</sub> , and unidentified material detected at interface
	4400	10	24	No adherence; UO detected at inter- face
HfB <sub>2</sub>	4700	40	62	Extensive interactions; HfB <sub>2</sub> and UO <sub>2</sub> detected in liquid phase
	4500	10	32	No adherence; UO detected at inter- face
TiB <sub>2</sub>	4700	40	73	Slight adherence; UO detected in liquid phase
	4500	10	25	No adherence; UO detected at inter- face
TaB <sub>2</sub>	4500	10	29	Slight adherence; UO detected at interface
	4000	4x10 <sup>-5</sup>	26x10 <sup>-5</sup>	No adherence; UO and UB <sub>2</sub> detected at interface
ThB <sub>4</sub>	4200	40	83	Strong adherence; UB <sub>2</sub> and UB <sub>4</sub> de- tected in liquid phase

## V. APPLICATIONS

The use of diborides is limited primarily by the absence of ductility. They have attracted attention because of their higher oxidation resistance at high temperatures in comparison with carbides and nitrides, as well as their excellent chemical resistance to aggressive media, and other properties important for modern technology. The applications of primary interest for this report are concerned with the aerospace field. Other applications are provided for general interest.

Nuclear: Preliminary studies (97) on behavior during neutron irradiation showed that diborides exhibit better dispersion qualities and superior retention of helium than  $B_4C$ . This study may lead to the use of diborides for reactor control applications. Since borides are resistant to the action of molten silicon, aluminum, copper, tin, magnesium, and fluorides they might be used in heat exchanges in the atomic power industry (98).

High Temperature Vacuum Applications: Important parameters to consider for high temperature vacuum uses is that the material possess minimum vapor pressures and evaporation velocities. Examples of direct application of these materials would be for vacuum resistance furnaces, thermocouples, and components for aerospace vehicles. Campbell states that the borides of the transitional metals should be considered as the best refractory materials to be used in vacuum at temperatures exceeding 2500°C (23).

Rocket Nozzles: The borides of zirconium and titanium have shown some promise for rocket nozzle applications. Nozzles up to 6-inch diameter have been produced. Lynch studied resistance of refractory materials for rocket nozzle inserts exposed up to 20 seconds in environment of aluminized solid propellants and found that the order of best resistance to rocket environment was refractory metals, high-density graphites, carbides, borides, nitrides, and oxides. (99).

Failure of the borides occurred either by thermal shock or by abrasion in the throat of a nozzle.

Combustion Chambers: Diborides may possibly be used for combustion chambers, but to date size and shape limitations of processing equipment have not been established. Coatings of diborides have been used as linings in combustion chambers. Chromium boride has proven to be quite successful for a lining material (100).

Gas-Turbine Blade Applications: A test was performed on turbine blades made of  $ZrB_2$  which illustrated that certain additions to the pure diboride improved its thermal shock and oxidation resistance. No conclusions were made from the study by Hoffman, but it was shown that the oxidation of a 97.5 percent  $ZrB_2$  plus 2.5 percent boron cermet body was very slight after 8.3 hours at temperatures up to 2000°F (101).

Re-Entry Applications: Coating of hafnium, zirconium, and thorium borides on refractory metals have been evaluated for re-entry applications. As for structural ceramic bodies of diborides for this type of application, no investigations have been performed (102).

Industrial Applications: Shield tubes of  $ZrB_2$  for immersion thermocouples. Sintered shield tubes having a porosity of 5-12 percent were tested in molten cast iron, steel, brass and bronze. When tested during tapping of cast iron in a blast furnace, they withstood 15 tappings or a total immersion of 10 hours 53 minutes. In an open-hearth furnace with basic lining, shield tubes are corroded by basic slags and destroyed after 30-40 minutes. In well open-hearth furnaces, shield tubes withstood 2 hours immersion in molten steel. They withstood 86 hours in molten brass and bronze at 850 / 50°C (103).

$ZrB_2$  is used for electrodes in the electrolysis of melts (104). This material has also been used effectively in high temperature burner parts (105).

Borides can also be used for fabrication of nozzles for atomization of fused metals, components of glass furnaces, boats for evaporation of over-heated metals in vacuum in metallization, and tubing for transfer of molten metals.

Girard (106) examined a number of refractory materials to determine their possible usefulness as materials for crucibles for melting, fining, and drawing high-silica glass compositions. Niobium diboride gave the most promising results for this use (27).

The diborides rate among the hardest materials synthetically produced. Therefore, they can be of use as special cutting tools, wear resistant surface and high-temperature ball and roller bearings.

Electronic Devices:  $ZrB_2$  and  $TaB_2$  have been tried by Lofferty (107) to be used for electron guns. They were found to be quite effective in electron emission.

Foamed Diborides: A study recently performed for the United States Air Force showed that good foam bodies could be produced of titanium, tantalum, and zirconium borides. Foams of niobium diboride were also made, using  $Nb_2O_5$  plus boron carbide (39).

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**APPENDIX I**  
**SELECTED ABSTRACTS**  
**(Articles published since 1959)**

PERIODICAL: WADD TR 60-52, March 1960, 24p  
SUBJECT: Research Investigation to Determine the Optimum Conditions for Growing Single Crystals of Selected Borides, Silicides and Carbides  
AUTHOR: Kiffer, A. D., Linde Company, Division of Union Carbide Corporation  
ABSTRACT: This work was undertaken to produce selected crystals in the refractory hard metals class for mechanical and other property determinations. A Verneuil-type process using an arc heat source and argon shield gas was employed. Single crystal boules of titanium diboride and tungsten disilicide, 1/4-inch diameter and up to 4-1/2-inches long, were made. Most of them cracked upon cooling. The largest single crystal pieces recovered were 1/4-inch diameter and over 1/2-inch long. Dimolybdenum carbide boules had large sections of a "single crystal"  $\text{Mo}_2\text{C}$  matrix containing about 10 percent by volume of another phase distributed uniformly through it. No  $\text{Mo}_2\text{C}$  single crystal pieces free from this phase were made. In very limited work with ditungsten pentaboride only polycrystalline boules were produced. A major problem was encountered in getting powders suitable for Verneuil-type crystal growth. Best results were obtained from compounds prepared by fusing together commercially available pure elements and crushing the lumps into a suitable particle size fraction. Process improvements and purer powders are required to produce better quality  $\text{TiB}_2$  and  $\text{WSi}_2$  crystals. More experimental information is required on the molybdenum-carbon and the tungsten-boron systems.

PERIODICAL: ASD TR 61-350, October 1961  
SUBJECT: Investigation of Single-Crystal and Polycrystalline Titanium Diboride: Metallographic Procedures and Findings  
AUTHORS: Lynch, C. T., 1st Lt., Vahldiek, F. W., Mersol, S. A., and Underwood, C. R., Aeronautical Systems Division  
ABSTRACT: Single-crystal and polycrystalline  $\text{TiB}_2$  was examined to develop applicable metallographic techniques for sectioning, mounting, grinding, polishing, and etching of  $\text{TiB}_2$  specimens. This work demonstrates the usability and practicability of using various SiC papers together with different grades of diamond paste on polishing wheels in preference to using cloths. It has been found that  $\text{H}_2\text{SO}_4$  as a constituent of etchants, produces more reliable and more consistent results than HF. The same is true of  $\text{H}_2\text{SO}_4$  when used as a constituent of electrolytes. Single-crystal  $\text{TiB}_2$  was found to have a type of Widmanstätten structure while polycrystalline  $\text{TiB}_2$  had a "needle-like" pattern.

PERIODICAL: Tsvetnyye Metally, (USSR), Nr. 11, pp 48-50, 1959  
SUBJECT: Production and Some Properties of Hafnium Boride  
AUTHORS: Paderno, Yu. B., Serebryakova, T. I., and Samsonov, G. V.  
ABSTRACT: Considerable work has been carried out on titanium and zirconium borides. Little study has been made of hafnium boride, but preliminary investigations show it has even better properties. There is probably only one stable compound - the diboride with  $\text{AlB}_2$  type structure. It has been obtained by precipitation from the gas phase. In the present work it was produced by the reduction of hafnium oxide by boron or boron carbide in a vacuum furnace. The relation of the free energy with temperature is -

$$P = 358.2 \times 10^3 - 175.05T$$

$$P = 91.9 \times 10^3 - 39.1T$$

for reduction by boron carbide and boron respectively. The reduction with carbide takes place at somewhat higher temperatures than with boron. At a pressure of  $10^{-1}$  mm mercury at 1300 to 1600°C, chemical analysis showed it was the stoichiometric diboride. X-ray analysis showed the cell to be  $a = 3.137$  and  $c = 3.469$  agreeing with the literature. Hot pressing was carried out at 2650° for 5 minutes with a load of 150 Kg/cm<sup>2</sup>. The minimum porosity obtained was 15.1 percent. The electrical resistance of the compound was 8.8 micro ohm/cm agreeing with the literature when porosity is taken into account. The microhardness was 2900/500 Kg/mm<sup>2</sup>. At temperatures above 650 to 700°C, an oxide film was formed on the compound.

PERIODICAL: U. S. Patent No. 2,998,302, 29 August 1961, Union Carbide Corp.  
 SUBJECT: Preparation of Titanium Diboride  
 AUTHORS: Mercuri, Robert A., Finn, John M., Jr., and Nelson, E. M.  
 ABSTRACT: The process comprises blending titanium dioxide of a particle size < 100 mesh with boric oxide of > 60 mesh, adding the blend to a molten sodium bath at 450° to 800°C, agitating the bath until the reaction is complete, cooling the mixture, and recovering titanium diboride of < 50 particle size and of 95 percent purity.

PERIODICAL: U. S. Patent No. 3,004,830, 17 October 1961  
 SUBJECT: Method of Producing Metal Borides  
 AUTHOR: Orne, Nils  
 ABSTRACT: The method comprises forming in a vertical electric arc furnace container a cup-shaped charge of a finely comminuted mixture of at least one of the transition metals, a boric acid component, and carbon, igniting an electric arc to melt the boric acid, to vitrify the wall of the cavity, and to dehydrate the boric acid, the composition of the mixture being such that a protective monoxide atmosphere of superpressure is maintained in the cavity, and smelting a successively increasing boride lump of the reduced metal in the bottom of the cavity.

SUBJECT: Zirconium Diboride Prepared Directly from Zircon  
 AUTHORS: McMullen, J. C., and McKee, W. D., Carborundum Company  
 ABSTRACT: Commercial exploitation of the very refractory zirconium diboride has been inhibited by the high cost of manufacture. Contributing to this high manufacturing cost has been the supposed necessity of using, in the final ZrB<sub>2</sub> yielding reaction, ingredients already expensive by reason of previous processing from the mineral source. In particular, Si-free zirconium sources, such as the metal, oxide, or carbide have been used. In the experiments described, zircon was reacted with boric oxide and carbon in a submerged electrode arc furnace, yielding a reasonably pure zirconium diboride in a one-step process.

The reaction depends on the volatility of silicon monoxide at the temperatures employed. Although other proportions provide somewhat better purity and yield, reactants in the stoichiometric proportions indicated by the following equation can be used:  $\text{ZrSiO}_4 + \text{B}_2\text{O}_3 + 6\text{C} \rightarrow \text{ZrB}_2 + 6\text{CO} + \text{SiO}$ .

**SUBJECT:** Pyrolytic Synthesis of Refractory Borides  
**AUTHORS:** Gannon, R. E., Vasilos, T., Folweiler, R. C., Avco Corporation  
**ABSTRACT:** The synthesis of refractory borides by vapor phase decomposition has been investigated. Effects of such process variables as deposition temperature, flow rates, and stoichiometry on the microstructure of the deposited boride have been studied. Photomicrographs, mechanical properties and deposition rates of the pyrolytic borides are shown.

**SUBJECT:** Method for the Production of Zirconium Boride  
**AUTHORS:** Espenschied, Helmut, National Lead Company  
**ABSTRACT:** The method comprises admixing an uncalcined zirconia hydrate pulp as precipitated from a basic zirconia salt solution in an amount equivalent to one mole on a zirconium oxide basis, 5 moles of carbon, and boric acid in an amount equivalent to two moles of boron oxide to form a slurry, agitating the slurry to form an intimate mixture, drying the mixture, and then heating it in an inert atmosphere to a temperature sufficiently high to complete the reaction between the materials and produce finely divided zirconium boride having a particle size of 1 to 20.

**PERIODICAL:** Report No. WAL 766.41/1, August 1961  
**SUBJECT:** Pyrolytic Refractory Materials for Solid Fuel Rocket Motor Applications  
**AUTHORS:** Francis, R., Flint, E. P., Arthur D. Little, Incorporated  
**ABSTRACT:** Results of an experimental program devoted to the development of refractory materials formed by pyrolytic processes are described. In this regard the relative merits of various pyrolytic techniques and furnace designs are critically evaluated, and optimum conditions for the formation of pyrolytic graphite and pyrolytic boron nitride have been investigated. Relevant properties of pyrolytic graphite and pyrolytic boron nitride are compared, and application of the principles derived has resulted in the formation of several large sound shapes of these materials. Exploratory experiments on the formation of other pyrolytic systems are also described.

**PERIODICAL:** WADC TR 59-654, December 1959  
**SUBJECT:** Synthesis of New High Temperature Materials  
**AUTHORS:** Engelke, J. L., Halden, F. A., Farley, E. P., Stanford Research Institute  
**ABSTRACT:** A number of mixed transition metal carbides, borides and nitrides were prepared and examined in terms of melting point, structure, and oxidation resistance. None of the measured melting points was higher than the value reported for  $\text{HfC}^{0.4}\text{TaC}$  ( $3940^\circ\text{C}$ ). The melting point for a series of solid solutions between HfC and HfC increased regularly with hafnium content.

PERIODICAL: Izvestiya Vysshikh Uchebnykh Zavedeniy - Chernaya Metallurgiya, Nr. 3, pp 13-16, 1960

SUBJECT: Thermodynamics of Chrome Diboride

AUTHORS: Krestovnikov, A. N., Vendrikh, M. S.

ABSTRACT: The effective heat absorbing capacity of Cr and B in  $\text{CrB}_2$  was calculated separately using Lindemann's formula for finding the natural vibration frequencies of Cr and B atoms; Debye function tables were used for calculating the atomic heat absorbing capacity of Cr and B and the isochoric heat absorbing capacities found for  $\text{CrB}_2$  in accordance with Neumann's and Kopp's law, and the isochoric capacities were converted into isobaric ones using the Nernst equation. The calculated heat absorbing capacities were compared with values determined by the authors in experiments with a water calorimeter. The values found per Debye and as measured coincided in the studied temperature interval (300-800°K) but differed considerably at higher temperature, which can be explained by an additional heat effect and must be yet experimentally proven. It is supposed that the real heat absorbing capacity curve for  $\text{CrB}_2$  corresponds to a second order parabola with slight curvature. The values for deep and low temperatures (23-300°K) were calculated per Debye and extrapolated further to absolute zero by the  $C_p/T - f(T)$  curve, and the standard entropy of  $\text{CrB}_2$  found to be  $S_{298}^\circ = 9.32$  cal/mol. degr., and the entropies of chrome, boron, chrome diboride, and of  $\text{CrB}_2$  were calculated. These data were used for finding the formation entropy of  $\text{CrB}_2$ . The standard formation heat of  $\text{CrB}_2$  (formation enthalpy,  $\Delta H$ ) having been found widely different by different authors (varying from 19.00 kcal/mole per G. V. Samsonov to 47.00 per O. Kubashevskiy and E. Evans the value 30.00 kcal/mol has been accepted for calculations, and the equation of the dependence of  $\Delta H_f^\circ$  on temperature was found:  $\Delta H_f^\circ = 29845 - 0.622T + 2.005 \cdot 10^{-3}T^2 - 0.44 \cdot 10^{-5}T^{-1}$ . Taking the  $\text{CrB}_2$  formation heat and entropy, its free energy (isobaric potential) was calculated.

TEMPERATURE IN °K

Thermo- dynamic Functions	298	500	1,000	1,500	2,000	2,173
$\Delta H$	-30,000	-29,743	-28,506	-26,290	-23,091	-21,747
$\Delta Z$	-30,071	-30,086	-31,122	-32,726	-35,315	-36,436

PERIODICAL: V sb.: Bor. Tr. Konferentsii po Khimii Bora i Yego Soyedineniy. Moscow, Goskhimizdat, pp 5-18, 1958

SUBJECT: On the Present State of Thermochemistry and Thermodynamics' of Boron and some Borides

ABSTRACT: The necessity is noted of collecting accurate thermochemical and thermodynamical data on boron and its compounds. The attention of thermochemists is drawn to the complexity of the reaction of boron and boride burning, the possibility of errors is indicated in the determination of combustion heats due to the neglected phase composition of the initial and final components of the reaction, the presence of admixture in the boron samples and the incomplete

burning of auxiliary fuel substances in the mixture with boron or boron-containing substances. In the determinations of combustion heats of boron compounds the subjection of the combustion products to phase, x-ray and ultramicrochemical analyses is recommended. The values of the formation heats and the average dissociation energies of several gaseous boron derivatives were cited according to the latest literature data. It was noted that Brewer's and Haraldsen's data on the formation heats of borides (RZhKhim, Nr. 9, 29883, 1957) may have an error of up to 10 kcal/mole due to the assumption that in the reactions investigated by these authors  $\Delta S$  and  $\Delta c_p$  are negligibly small. The standard entropies are calculated for the formation of diborides of Ti, Zr, Nb and Ta which are -4.9, -5.4, -4.9 and -4.4 entropy units, respectively. The possibilities of the approximate evaluation of the thermochemical and thermodynamic data for boron compounds were discussed.

PERIODICAL: L: Optika i Spektroskopiya, Vol 8, Nr. 3, pp 410-412, 1960 (USSR)

SUBJECT: The Emissivities of Powders of Some Refractory Compounds

AUTHORS: Serebryakova, T. I., Paderno, Yu. B., Samsonov, G. V.

ABSTRACT: The authors report measurements of the emissivities of powders of borides, carbides and nitrides of refractory and rare-earth metals. Measurements were carried out with an instrument which simulated closely an absolute black body. A tantalum cylinder (20 mm diameter, 50 mm height) served as a heater. Inside the cylinder there was another smaller tantalum cylinder (8 mm diameter, 20 mm height) which was placed concentrically with the cylinder. In each of the cylinders there was a small aperture and these apertures were aligned horizontally. The lower ends of the two tantalum cylinders were fixed to a molybdenum plate which was pressed against a cylinder by a spring. The inner cylinder was coated with 100μ thick layer of paste prepared from a fine powder (particles of 2-3μ diameter) of the refractory material mixed with a binder. Temperature of the inner cylinder surface (the brightness temperature,  $T_b$ ) and temperature in the aligned apertures (the true temperature,  $T_t$ ) were measured with an pyrometer. Absorption in the glass bulb was found to be negligible. The emission intensities were measured at 650 mμ and the emissivities were calculated using the following formula:

$$\epsilon_{\lambda} = \frac{c}{\lambda} \left( \frac{1}{T_t} - \frac{1}{T_b} \right)$$

where  $c = 1.438$  cm/deg and  $\lambda$  is the wavelength. The measured emissivities of pure tantalum at temperatures from 800 to 2000°C agreed well with the published values. The measured emissivities of LaB<sub>6</sub>, NbB<sub>6</sub>, TiC, SmB<sub>6</sub>, GdB<sub>6</sub>, YB<sub>6</sub>, ZrB<sub>2</sub>, HfB<sub>2</sub>, B<sub>4</sub>C, Cr<sub>3</sub>C<sub>2</sub> and BN powders at temperatures from 850 to 1650°C were given.

PERIODICAL: J. Phys. Chem. Solids, Vol 4, pp 118-127, 1958

SUBJECT: Hall Effect and Electrical Conductivity of Transition-Metal Borides

AUTHORS: Juretschke, H. J., Steinits, R.

ABSTRACT: The room-temperature resistivity and Hall constant of the diborides of the fourth to sixth-column transition metals and their solid solutions have been measured in order to clarify the electronic structure of these compounds.

Since the experimental samples, prepared from powders, were usually porous, extrapolation procedures have been developed to relate the electrical properties measured on porous samples to those to be expected at full density. The results thus extrapolated indicate that all these compounds have a similar band structures, the substitution of one transition metal for another changing mainly the occupation of the conduction band. This conduction band is of standard shape; it is nearly empty for fourth-column transition metals, and is filled to about one electron per cell upon substituting a fifth-column metal. If the band structure of these compounds derives from that of the transition metals, the results suggest that the usual s-d band overlap is here considerably reduced, and that the d-band are completely filled by the contribution of three electrons from each boron atom. This makes the main conduction band an s-band. Such an interpretation is in accord with a number of other characteristic properties of these compounds.

APPENDIX II  
SELECTED ARTICLES



SELECTED ARTICLE NO 1  
CERAMIC ENGINEERING  
PRESSING AND SINTERING OF BORIDE POWDERS (Ref: 34)

B.N. Babich  
K. I. Portnoy  
Professor G.V. Samsonov

(Translation by S.A. Mersol)

INTRODUCTION

Greater utilization of products made of borides or of alloys having a boride base (1, 2) made it necessary to establish a program for studying the powder metallurgy of these compounds.

Our investigation started with a study of reference 3. It was shown there that powders of hard materials sinter by means of the gradual breakdown of the uneven portions of the grains which are in contact with each other during their mutual migration. A determination of the degree of brittleness of powders of hard compounds is proposed, and the connection between the brittleness and the stability of the bond in the crystal lattice of the compound is indicated (3).

Chiotti (4) used the method of the separate pressing and sintering of specimens made of carbides of refractory metals. To facilitate sintering, he made use of the formation of the liquid phase with the addition of iron (up to 8 percent) or iron salt (up to 2.5 percent); the final content of the impurity in the specimen did not exceed 0.5 percent.

In the sintering process of refractory compounds (carbides and oxides), the main reason for the shrinkage of sufficiently pure compounds during sintering is that during heating the particles attain a plasticity, which is sufficient for the grains to be pulled into pores under the influence of the forces of surface tension and in the direction of the center of gravity of the pellet (5).

This process, often accompanied by recrystallization, starts above a homologous temperature of 0.8 ( $T_{\text{sintering}} : T_{\text{melting}}$ ). The porosity of the sintered object can be reduced to values of less than 10 percent. This theory agrees with G.A. Myerson's theory of sintering, developed for plastic metals (6).

We investigated the conditions of pressing and sintering of  $\text{TiB}_2$  and  $\text{CrB}_2$  powders as well as those of the titanium and chromium boride alloy (the ratio of molar concentrations of  $\text{TiB}_2 : \text{CrB}_2 = 4 : 1$ ).

The initial  $\text{TiB}_2$  and  $\text{CrB}_2$  powders were prepared in vacuum. Then  $(\text{Ti, Cr})\text{B}_2$  was prepared from the specific mixture of these borides at  $1700^\circ\text{C}$  for one hour in vacuum.

The average particle diameter of the pellets of all three powders measured from 2 to 3 microns. Their loose-packed weights and their close-packed weights are shown in table 1.

TABLE I  
THE LOOSE - PACKED WEIGHT AND THE CLOSE - PACKED WEIGHT OF BORIDE POWDERS

BORIDE	LOOSE - PACKED WEIGHT	CLOSE - PACKED WEIGHT	$\frac{\gamma \text{ CLOSE - PACKED}}{\gamma \text{ LOOSE - PACKED}}$
TiB <sub>2</sub>	0.80	1.24	1.55
CrB <sub>2</sub>	1.05	1.64	1.57
(Ti,Cr)B <sub>2</sub>	0.97	1.53	1.58

### PRESSING

The specimens were pressed in a steel cylindrical die on a hydraulic press at pressures of from 0.5 to 8 tons/cm<sup>2</sup>. For all tests the specimens had a diameter of 15 mm and were from 6 to 10 mm high. A study of the pressing procedure (9) involved a determination of the influence of the maintained pressure on the density of the pressed pellets by measuring their elastic properties and by studying the influence that interstitial wear or rubbing had had on their density.

The pellets proved to be of low strength, and the tremendous wear of the dies used for dry pressing made it necessary to mix plasticizers with the powders. The following plasticizers were used: a solution of synthetic rubber in gasoline (400 ml of 4 to 5 percent solution to 1 kg of the powder), a solution of Na<sub>2</sub>SiO<sub>3</sub> in alcohol (the content of Si in the mixture was 1 percent), and a solution of FeCl<sub>3</sub> in alcohol (the content of Fe in powder was 1 percent).

The density of the pressed specimens was determined by the pressing rate and the applied pressure. To test the pellets' elasticity, the distance from the base of the die to the upper end of the die (the plunger) was measured and considered its indicator; the correction for the elastic compression of the plunger under load was entered, and the height of the pellet after pressing was measured.

None of the above listed plasticizers markedly improved the compressibility; however, the strength of the pellets was greatest when the FeCl<sub>3</sub> solution was used, and was therefore used in subsequent experiments.

Figure 1 shows the results of pressing at various compacting pressures. As the data indicates, TiB<sub>2</sub> performed better than CrB<sub>2</sub>. Lamination phenomena during pressing started in the pressure range above 3 to 4 tons/cm<sup>2</sup>.

Figure 2 shows a compacting pressure diagram in logarithmic coordinates,  $\log p_{sp} - \log \beta$ , where  $\beta$  is the relative volume  $\beta = \frac{\gamma_{compact}}{\gamma_{pellet}}$ , from which it follows that the pressing process is well expressed by the straight lines:

$$\text{For TiB}_2, \log p_{sp} = -11.07 \log \beta + 3.02$$

$$\text{For CrB}_2, \log p_{sp} = -10.48 \log \beta + 3.25$$

$$\text{For (Ti,Cr)B}_2, \log p_{sp} = -11.29 \log \beta + 3.24$$

where  $p_{sp}$  is specific pressure.

The continuance of pressure from 15 to 60 seconds does not have any effect on the density of the pressed pellet or briquette.

The continued process of rubbing pre-pressed specimens over the sieve 0105H with subsequent pressing at the same pressure allows the density of the pressed samples to increase for about 5 percent, whereby the greatest effect is produced by the first rubbing.

Figure 3 shows the results of the elasticity determination. When the results are compared with those obtained by an analogous investigation performed on metallic powders (9), it is notable that the length of time for which the powders were subjected to the pressure had no effect on the density of the boride pellets. This proves the practically complete nonplasticity of the pellets and the conservation of a highly strained state after pressing.

The relative elasticity of borides after pressing is in complete agreement with the high hardness of borides, since by comparison (9) the very hard tungsten carbide has a tremendous elastic effect after pressing. This also corresponds to the data of work (10). The elastic effect on the borides increases with the increase of the pressure to from 1 to 2 tons/cm<sup>2</sup>. The decrease in magnitude of the elastic effect, which occurs at very high pressures, is due to the breakdown and hardening of the pressed pellets and to the distribution of fine-grained broken-off particles in-between larger unbroken particles. At still higher pressures, the elastic effect again increases; this is accompanied simultaneously by lamination phenomena. Technically, it is possible to consider the compacting pressure of 3 tons/cm<sup>2</sup> as the most favorable one, and at this pressure it is expedient to employ multiple pressing techniques.

In our studies of borides the most pronounced elastic effect in the powder borides occurred in the hardest boride, namely, TiB<sub>2</sub> (3370 kg/cm<sup>2</sup>), and in case of the solid-solution boride, in (Ti, Cr)B<sub>2</sub> (about 3800 kg/mm<sup>2</sup>). The elastic effect on CrB<sub>2</sub>, whose hardness is 1800 kg/mm<sup>2</sup>, is considerably smaller.

## SINTERING

The conditions of sintering were studied by first compacting the pellets under the chosen pressure of 3 tons/cm<sup>2</sup>. The sintering was performed at a pressure of 0.1 mm Hg in a vacuum tube furnace having a graphite heater (11). To determine the optimum sintering temperature, the specimens were sintered within the 1700° to 2400°C range for one hour.

The specific gravities of the sintered specimens were determined by hydrostatic suspension, and the linear shrinkage by the resultant heights (table 2).

TABLE 2  
RESULTS OF THE SINTERING OF BORIDES

BORIDE	CHARACTERISTICS OF THE MATERIAL	SINTERING TEMPERATURE IN °C							
		1700	1800	1900	2000	2100	2200	2300	2400
TiB <sub>2</sub>	DENSITY IN G/CM <sup>3</sup>	—	3.31	3.49	3.49	3.47	3.63	3.81	4.04
	RESIDUAL POROSITY IN %	—	25.5	21.6	21.6	22	18.4	14.3	9.1
CrB <sub>2</sub>	DENSITY IN G/CM <sup>3</sup>	3.52	3.83	4.01	4.25	4.30	M E L T E D		
	RESIDUAL POROSITY IN %	37.1	31.6	28.4	24	23.2			
(Ti,Cr)B <sub>2</sub>	DENSITY IN G/CM <sup>3</sup>	—	3.70	3.86	—	3.84	3.91	4.20	4.45
	IN %	—	22.4	19	—	19.4	18	11.9	6.7

From the table we see that the sintering process occurs in two stages: (1) minor density increase at the temperature up to 2100° or 2200°C, and (2) intensive density increase above 2100° or 2200°C. It is evident that in the second stage the plasticity of borides becomes sufficiently great to have surface tension overcome the strength of the particles. In all cases the reduced temperature at the beginning results in an increased density of from 0.7 to 0.8. The optimum sintering time was determined by holding Tib<sub>2</sub> and the solid solution (Ti, Cr)B<sub>2</sub> at 2300°C; CrB<sub>2</sub> was held at 2000°C (table 3).

TABLE 3  
THE CORRELATION BETWEEN THE BORIDE SPECIMENS  
DENSITY AND THE SINTERING TIME

BORIDE	SINTERING TEMPERATURE IN °C	SINTERING TIME IN MIN.	DENSITY IN G/CM <sup>3</sup>	RESIDUAL POROSITY IN %
TiB <sub>2</sub>	2300	30	3.72	16.4
		60	3.80	14.3
		120	3.81	14.2
		240	3.79	14.4
CrB <sub>2</sub>	2000	30	4.18	25.6
		60	4.25	24
		120	4.26	23.9
		240	4.26	23.9
(Ti,Cr)B <sub>2</sub>	2300	30	4.16	12.5
		60	4.20	11.9
		120	4.20	11.9
		240	4.22	11.6

At the sintering temperatures selected the equilibrium between the stability of the particles and the surface tension is established rather rapidly; the higher the sintering temperature, the faster it progresses. In all cases, but especially in the case of  $\text{TiB}_2$  and  $(\text{Ti}, \text{Cr})\text{B}_2$ , the low porosity of the specimens resulted from sufficiently high temperatures. As the temperature was increased, the attainment of a porosity approaching zero did not present special difficulties.  $\text{CrB}_2$  is an exception, for its lowest porosity amounts to 23 percent and at the increased temperature (higher than  $2100^\circ\text{C}$ ), melting begins. (The melting temperature of  $\text{CrB}_2$ ,  $1900^\circ\text{C}$ , as often cited in literature, is incorrect. According to the data in references 12 and 13, it is at  $2200^\circ\text{C}$ . It seems that this discrepancy is due to the dissociation of  $\text{CrB}_2$  in the range of temperatures close to its melting point.)

## CONCLUSIONS

The densification process of  $\text{TiB}_2$ ,  $\text{CrB}_2$ , and  $(\text{Ti}, \text{Cr})\text{B}_2$  powders is described by the logarithmic correlation between the relative volume and the compacting pressure. The resultant elastic effects of the materials studied is rather high. The dependence of the elastic effect on pressure is connected with the high brittleness and nonplasticity of the borides.

The process for achieving increased densities in boride pellets by sintering consists of drawing particles into the pore spaces upon attainment of that temperature at which the forces of surface tension prevail over the strength of the particles which become plastic.

The possibility of using separate cold pressing and sintering instead of the complex and uneconomical method of hot pressing was demonstrated.

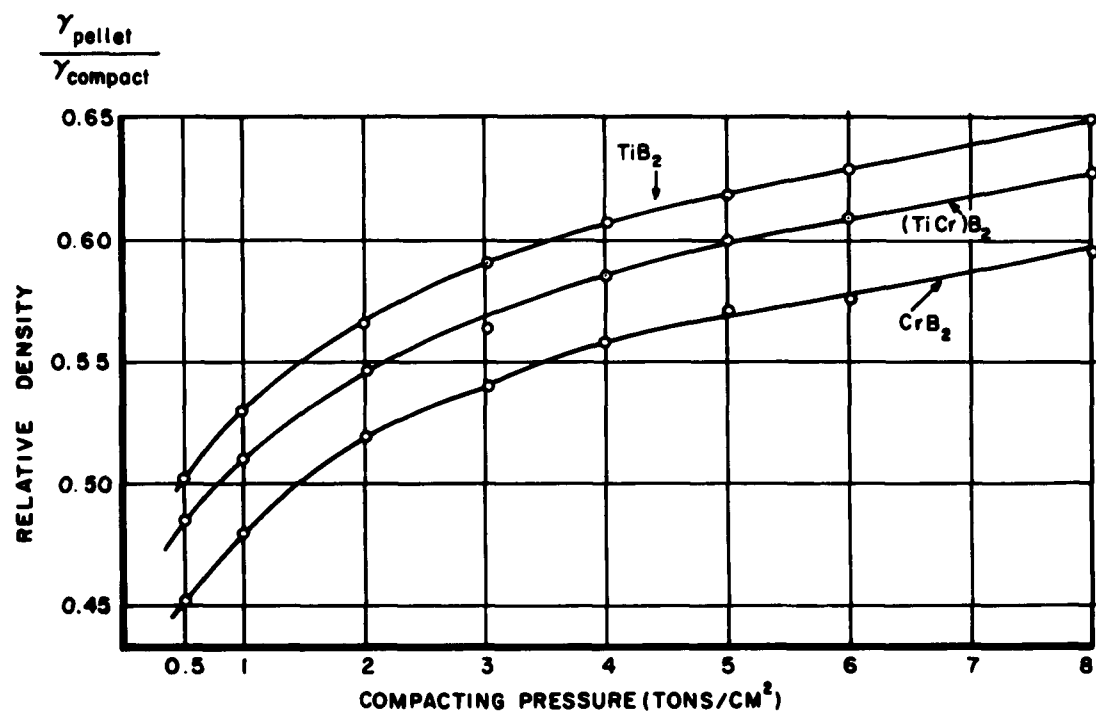


Figure 1. Correlation Between Relative Density and Compacting Pressure

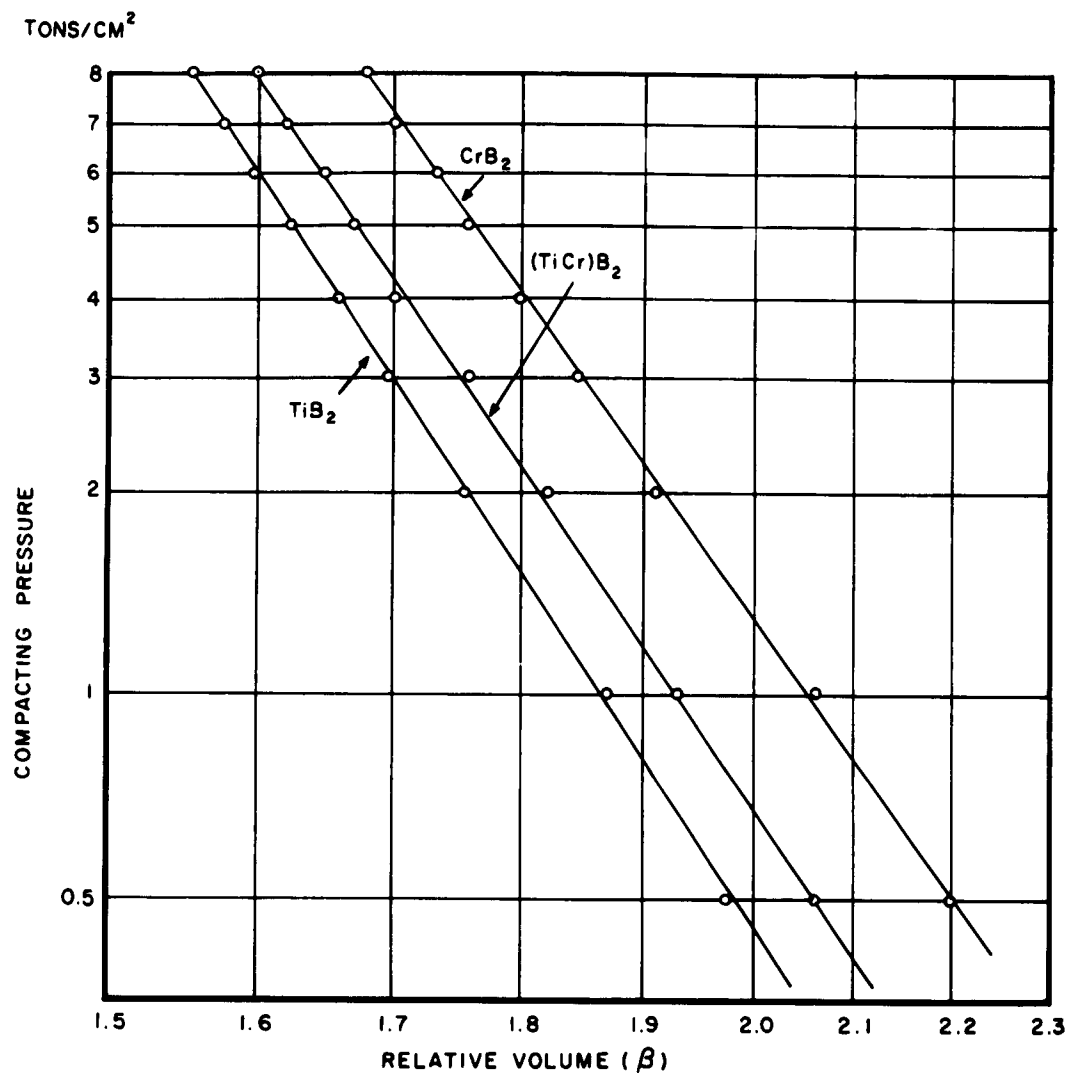


Figure 2. Correlation Between the Relative Volume and the Compacting Pressure

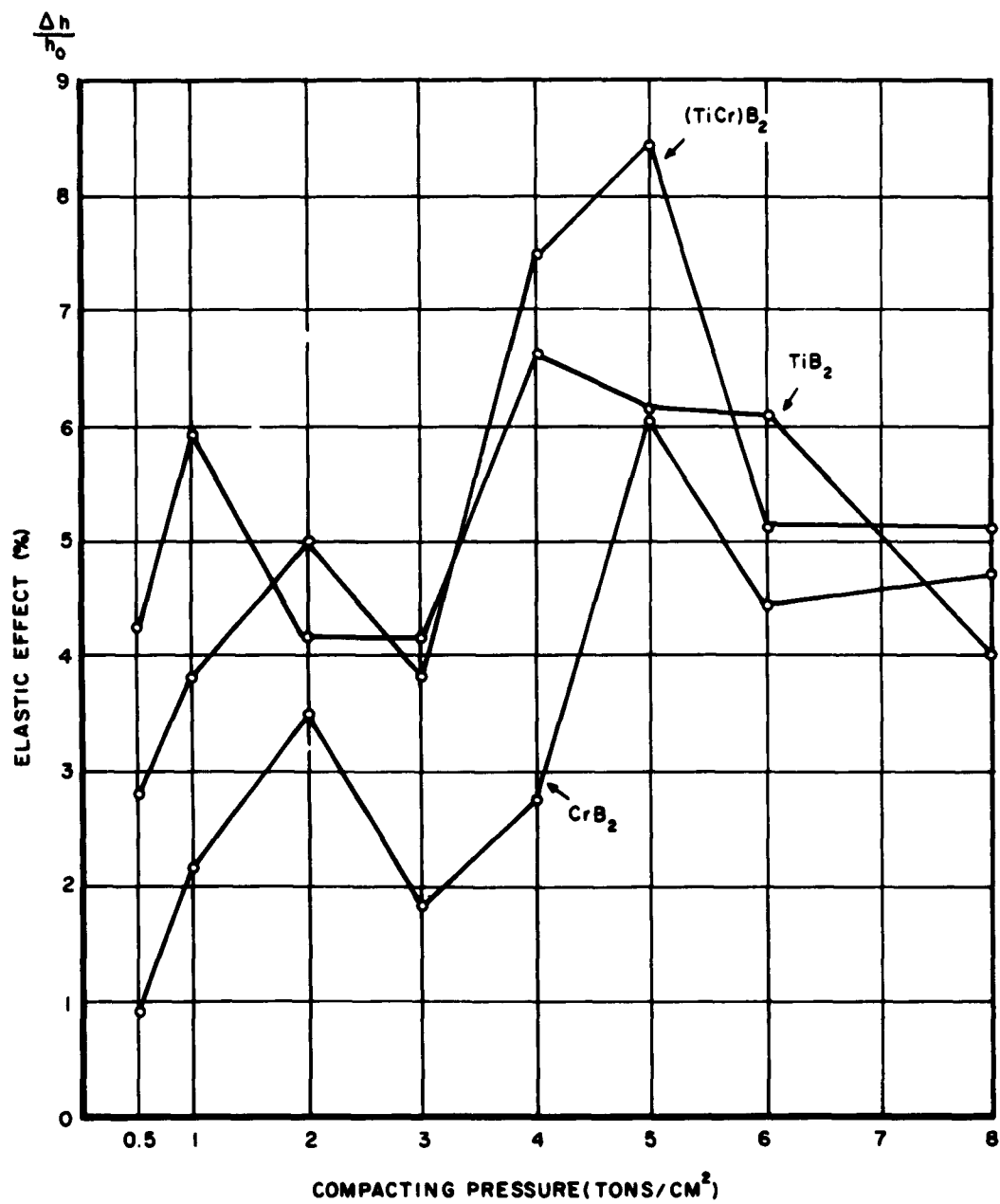


Figure 3. Correlation Between Elastic After-effect and Compacting Pressure



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## VACUUM THERMAL PREPARATION OF BORIDES OF HIGH-MELTING METALS

## NOTE

What follows is part of an article "Vacuum Thermal Preparation of Borides of High-Melting Metals" by G.A. Merson and G.V. Samsonov, translated from the Zhurnal Prikladnoi Khimii Vol. 27, No. 10, 1954, Moscow, pp 1115 to 1120.

## EXPERIMENTAL

A vacuum resistance furnace with a graphite heater [5] was used for performing the indicated reaction and is schematically illustrated in Fig. 1.

The heater was a tube made of electrode graphite with an internal diameter of 24 mm and a wall thickness of 1.5 mm, sealed between two molybdenum contacts placed on hollow brass conductors internally cooled by water.

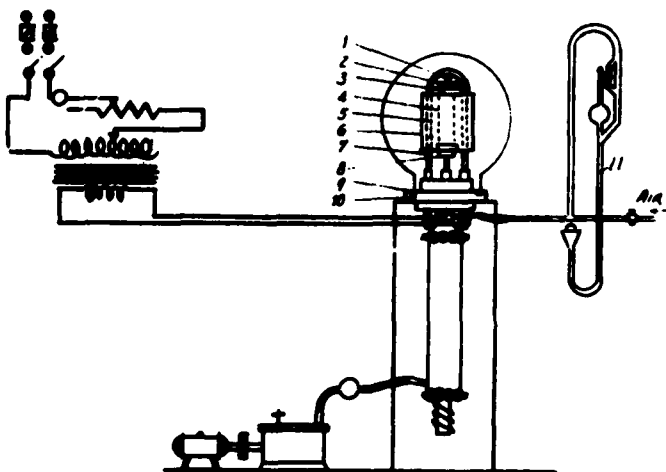


Figure 1. Vacuum resistance furnace. 1) Coil, 2) chamotte plate, 3) upper contact, 4) graphite vessel, 5) molybdenum shield, 6) glass hood, 7) electrode, 8) lower contact, 9) rubber ring, 10) furnace plate, 11) compression vacuum gauge.

In order to reduce the loss of radiant heat, the tube was shielded by concentrically placed graphite and molybdenum shields with apertures for optical temperature measurement. The tube was fastened to the water-cooled furnace bottom which had an annular depression with a rubber vacuum gasket for taking the vessel which was prepared of a special type of glass and could withstand heating to 400-500°.

The vacuum was produced with a VN-461 fore-pump and a T, VL-100 oil diffusion pump. The pressure in the furnace was measured with a compression vacuum gauge.

The charge was made according to the above noted reaction, and briquetted; the briquettes were placed in pairs in the heating tube on a ring made of boron carbide in such a way that the outer surfaces of the briquettes did not touch the graphite tube (Fig. 2).

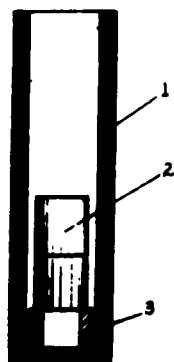


Figure 2. Placing the briquettes in the heater. 1) Graphite tube, 2) briquette, 3) graphite ring.

In this work, we investigated conditions for preparing the bromides of titanium, zirconium, vanadium, niobium, and tantalum; the starting substances were the oxides of these metals, boron carbide, and carbon black; compositions are given in Table 1.

Preparing titanium and zirconium borides. A tensiometric study of the reaction:  $2\text{TiO}_2 + \text{B}_4\text{C} + 3\text{C} = 2\text{TiB}_2 + 4\text{CO}$ , was made in a preliminary study of conditions for preparing titanium boride.

The experimental method consisted in gradually increasing the furnace temperature and measuring the pressure of the carbon monoxide evolved at the corresponding temperature; when a marked break in pressure was observed, the temperature was held constant until a time when the pressure did not reach some minimum which was constant for given temperature (bearing in mind the gas liberated from the metallic parts, the graphite, and the flask). A sharp increase in pressure may be caused only by the start of a reaction which takes place liberating CO or a mixture of  $\text{CO} + \text{CO}_2$  (depending on the temperature range). Thus, we may establish the temperature for the start of reaction at a given pressure and physical composition of the charge by an abrupt pressure change.

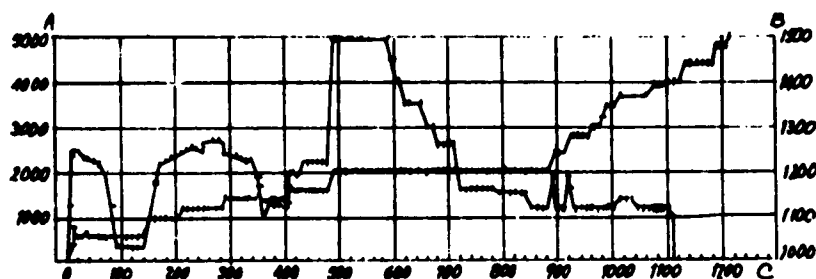


Figure 3. Tensiometric curves for the reaction:  $2\text{TiO}_2 + \text{B}_4\text{C} + 3\text{C} = 2\text{TiB}_2 + 4\text{CO}$ . A) Pressure (mm Hg); B) Temperature (°C); C) time (minutes).

TABLE 1

## Composition of Raw Materials for Boride Preparation

Material	TiO <sub>2</sub>	ZrO <sub>2</sub>	V <sub>2</sub> O <sub>5</sub>	Nb <sub>2</sub> O <sub>5</sub>	Ta <sub>2</sub> O <sub>5</sub>	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	SnO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	B	C
TiO <sub>2</sub>	98.25	-	-	-	-	0.75	-	Traces	-	0.08	-	-
ZrO <sub>2</sub>	0.35	97.90	-	-	-	0.14	Traces	0.43	-	-	-	-
V <sub>2</sub> O <sub>5</sub>	0.03	-	99.15	-	-	0.25	-	Traces	-	-	-	-
Nb <sub>2</sub> O <sub>5</sub>	0.27	-	-	98.90	0.65	0.10	-	-	-	-	-	-
Ta <sub>2</sub> O <sub>5</sub>	0.68	-	-	2.23	97.35	0.10	0.73	-	0.91	-	-	-
Carbon Black	-	-	-	-	-	-	-	-	-	-	-	99.9
B <sub>4</sub> C	-	-	-	-	-	-	-	-	-	-	78.20	21.70

Curves obtained by holding at temperatures corresponding to the pressure jumps are given in Fig. 3. As can be seen from these curves, three rather clearly expressed jumps in pressure take place; the first two of these correspond to the transition of TiO<sub>2</sub> into Ti<sub>2</sub>O<sub>3</sub> or Ti<sub>2</sub>O<sub>3</sub> into TiO, as was similarly shown in a previous study on conditions for reducing TiO<sub>2</sub> by carbon [5]. The third jump is observed at 1120°C (pressure ~ 2000 mm Hg) and evidently corresponds to the reaction:



According to the results of chemical analysis, the product obtained here has the following composition:

According to Formula			Found (%)
TiB <sub>2</sub> (in%)			
Ti	68.90		68.20
B	31.10		31.02
C	0.00		0.019
Total	100.00		99.239

The lower temperature limit for starting to obtain TiB<sub>2</sub> by the stated reaction under vacuum is 1100-1150°C (at the given degree of rarefaction of the furnace). In view of the long time required for conducting the reaction at this temperature, a higher temperature region was investigated ranging from 1200 to 1900° at intervals of 100° (holding for one hour at each).

The corresponding data are given in Table 2. Thus, at 1400° and above, titanium boride is formed in one hour, subsequently small changes in the product composition at higher temperatures do not exceed the limits of analytical error related to the difficulty of determining Ti and B when they are both present [6].

A study of the effect of holding time at 1400° (the last 3 experiments, Table 2), showed that reducing the holding time to 1/2 hour did not permit the reaction to proceed to conclusion; this can be judged by the significant quantity of unremoved carbon. Holding for over one hour was likewise inexpedient.

Similar reaction conditions were also established for the reaction preparing zirconium boride  $ZrB_2$ .

Roentgeno-structural analysis of powdered titanium and zirconium borides prepared by this procedure, performed using copper illumination showed a hexagonal structure for both compounds with lattice constants for  $TiB_2$  of  $a=3.020$  kx,  $c=3.217$  kx;  $c:a=1.065$  (according to the literature data [8] for pure titanium boride prepared synthetically from its elements,  $a=3.028$  kx;  $c=3.228$  kx;  $c:a=1.064$ ), and for  $ZrB_2$ ,  $a=3.172$  kx;  $c=3.538$ , and  $c:a = 1.115$  (according to literature data [8]  $a=3.170$  kx;  $c=3.533$  kx;  $c:a=1.115$ ). The identification was made graphically; the agreement must be regarded as satisfactory: for  $TiB_2$  all 11 lines for  $K_\alpha$  - radiation agreed.\*

TABLE 2

Chemical Composition of Products from Treating the  $2TiO_2 + B_2C + 3C$  Charge under Vacuum, as Dependent on Temperature and Time of Heating.

Temperature (°C)	Time (minutes)	Pressure (mm Hg)		Yield (%)	Chemical Composition (%)			
		initial	final		Ti	B	C Total	Total
1200	60	$3 \cdot 10^{-3}$	$4 \cdot 10^{-1}$	-	-	25.51	8.39	-
1300		$2 \cdot 10^{-3}$	$4 \cdot 10^{-1}$	-	-	28.93	1.41	-
1400		$3 \cdot 10^{-3}$	$3 \cdot 10^{-1}$	100.0	69.52	30.49	0.02	100.03
1500		$3 \cdot 10^{-3}$	$3 \cdot 10^{-1}$	100.0	69.70	30.53	0.019	100.25
1600		$3 \cdot 10^{-3}$	$4 \cdot 10^{-1}$	99.0	68.49	31.53	0.018	100.04
1700		$4 \cdot 10^{-3}$	$4 \cdot 10^{-1}$	98.0	69.52	30.92	0.019	100.46
1800		$3 \cdot 10^{-3}$	$4 \cdot 10^{-1}$	95.0	69.21	31.51	0.019	100.74
1900		$3 \cdot 10^{-3}$	$4 \cdot 10^{-1}$	95.6	69.64	30.62	0.024	100.28
1400	15	$2 \cdot 10^{-3}$	4.2	-	-	28.18	1.20	-
1400	30	$4 \cdot 10^{-3}$	1.0	-	-	31.50	1.24	-
1400	120	$3 \cdot 10^{-3}$	$2 \cdot 10^{-1}$	99.5	68.55	31.40	0.06	100.01

TABLE 3

Main Characteristics of Powdered Vanadium, Niobium, and Tantalum Borides Obtained by the Vacuum Thermal Method.

Boride	Chemical composition %						Lattice constants (Å)		c:a	Average particle size (μ)	Density
	V (Nb, Ta)		B		C <sub>Total</sub>	Total					
	Calculated	Found	Calculated	Found			a	c			
VB <sub>2</sub>	70.10	70.00	29.90	29.83	0.09	99.99	3.000	3.050	1.027	1.86	4.56
NbB <sub>2</sub>	81.04	1.14	18.96	18.95	0.17	100.26	3.080	3.304	1.073	1.90	6.80
TaB <sub>2</sub>	89.30	88.40	10.70	10.51	0.16	99.07	3.082	3.239	1.075	2.41	11.85

\* The photographs and calculations for lattice constants were performed by R.B. Kotelnikov.

The average particle size of titanium and zirconium boride powders prepared by the vacuum thermal method was to 2.2 and 2.3 $\mu$ , respectively, and about 70-80% was in the 1.5-3 $\mu$  range. Pycnometric determination of the powder density, performed under the microscope using benzene, gave the values:  $d_{\text{TiB}_2} = 4.44$  and  $d_{\text{ZrB}_2} = 6.24$ , as compared with those calculated from the lattice constants:  $d_{\text{TiB}_2} = 4.45$  and  $d_{\text{ZrB}_2} = 6.04$ .

Preparing vanadium, niobium, and tantalum borides. The process for preparing vanadium, niobium, and tantalum borides was exactly the same. The main characteristics of the products obtained are given in Table 3.

Preparing tungsten boride. In preparing tungsten boride by the vacuum thermal procedure, we are confronted with the high volatility of tungstic anhydride and its preliminary reduction to  $\text{WO}_3$  leading then to a reaction forming the boride at relatively low temperatures, and likewise with providing some excess  $\text{WO}_3$  to compensate its volatility in the vacuum furnace.

Tungsten boride prepared in this manner has a chemical composition close to  $\text{W}_2\text{B}_5$ , an average particle size of 2.4 $\mu$ , pycnometric density 11.96, and lattice constants  $a=2.00$  and  $c=13.80$  kx.

#### SUMMARY

1. A vacuum thermal procedure for preparing borides of high-melting metals by reacting the corresponding oxides with boron carbide and carbon black according to the scheme:



enables us to obtain, under comparatively simple experimental conditions, pure borides very close in composition to the compounds described by the formulas  $\text{MeB}_2$  or  $\text{Me}_2\text{B}_5$  with very little contamination from residual carbon (as a rule in quantities below 0.2%).

2. The possibility of preparing titanium, zirconium, vanadium, niobium, tantalum, and tungsten borides by the indicated method was demonstrated.

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## CHEMICAL RESISTANCE AND HYDROLYTIC DECOMPOSITION OF SOME TRANSITION METAL DIBORIDES ON REACTION WITH ACIDS

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Borides of transition metals, especially zirconium, titanium, and chromium diborides, have been attracting increasing attention from investigators over recent years as construction materials [1,2]. These substances, which have high melting points ( $\text{ZrB}_2$ ,  $3040^\circ$ ,  $\text{TiB}_2$ ,  $2980^\circ$ ,  $\text{CrB}_2$ ,  $2300^\circ$ ), good thermal and electrical conductivity, and comparatively high slag resistance, have been the subject of many investigations in various countries, including the Soviet Union [1,3-10]. The chemical resistance of these substances to various reagents has been investigated much less. Up to now there have only been fragmentary and often contradictory reports on this problem. Thus, in 1913 Wedekind [11] stated that zirconium boride, to which he assigned the formula  $\text{Zr}_3\text{B}_4$ , is decomposed by hydrochloric acid with the liberation of boron hydrides, while other authors said that it has considerable resistance to this acid.

According to the data of Kifer and Shvartskopf [2],  $\text{ZrB}_2$  only reacts weakly with hydrochloric acid, but more vigorously with  $\text{HNO}_3$ , a mixture of  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ , aqua regia, and hot sulfuric acid;  $\text{ZrB}_2$  dissolves readily in molten alkali metal carbonates, bisulfates, and hydroxides. Titanium diboride has even greater chemical resistance. It is also very resistant to oxidation by atmospheric oxygen. According to the same data [2], it is insoluble in hydrochloric and hydrofluoric acids, but dissolves readily in mixtures of  $\text{HNO}_3$  with hydrogen peroxide or sulfuric acid and in sulfuric acid alone with heating. According to the data of Andrieux and Marion [12], all chromium borides, including  $\text{CrB}_2$ , are resistant to nitric acid. According to the data of Campbell, Powell, et al. [13], chromium borides are some of the most slag-resistant compounds.

The first systematic investigation of the chemical resistance of powdered borides of transition metals, prepared by the boron carbide method, was carried out by Samsonov and his co-workers [14, 15]. As a result of an investigation of the chemical resistance of powdered titanium, zirconium, vanadium, niobium, tantalum, chromium, molybdenum, and tungsten borides to hydrochloric, nitric, sulfuric, phosphoric, perchloric, oxalic, and hydrofluoric acids (both concentrated and dilute), in the cold and at the boiling points, quantitative data were obtained characterizing the degree of solution of the powders investigated in the given media. The data obtained showed that all the borides, with the exception of niobium and tantalum borides, have a considerable solubility in acids, especially nitric acid. All the borides, with the exception of Nb, Ta, and Cr borides, dissolved in nitric acid at a high rate, even in the cold, while chromium boride dissolved in boiling nitric acid. Niobium and tantalum borides dissolved readily only in hydrofluoric acid and in concentrated sulfuric and phosphoric acids on heating. The same article gave interesting data on the solubility of borides in mixtures of acids with various additives and also on the solubility of borides in NaOH solutions of various concentrations. However, in this work no data were given on the chemistry of the processes occurring during the solution of borides of transition metals in various aggressive media. In the work of the authors of the given article on the hydrolytic decomposition of magnesium and beryllium borides [16-18], it was shown that the solution of these borides is accompanied by the liberation of a certain amount of boron hydrides and hydrogen.

TABLE 1

Composition of Borides According to Chemical Analysis Data [25]

Borides	Products synthesized by carbon reduction (in%)			Products synthesized by the boron carbide method (in %)			Products synthesized by the electrochemical method (in %)	
	Me	B	C	Me	B	C	Me	B
ZrB <sub>2</sub>	80.9	18.1	1.1	80.2	18.4	0.8	80	19.2
TiB <sub>2</sub>	68.9	28.5	1.3	68.4	29.6	1.0	69	30.8
CrB <sub>2</sub>	69.8	30.2	1.8	69.8	27.2	2.0	--	--

From the literature [19] it is known that even some extremely chemically resistant borides (for example, AlB<sub>2</sub> and CeB<sub>2</sub> form small amounts of boron hydrides on decomposition in acids. As has been mentioned already, it has been shown experimentally that zirconium boride [11] and transition metal borides liberate boron hydrides on solution in HCl. Therefore, it may be surmised that the solution of these borides in acids, which results in the formation of the corresponding metal salts and boric acid, passes through the intermediate stage of the formation of boron hydrides.

It may be surmised that the primary product of the hydrolytic decomposition of borides is borine, BH<sub>3</sub>. The substance is extremely reactive and has not yet been isolated in a pure form. On contact with water it is largely hydrolyzed to form B<sub>2</sub>O<sub>3</sub> or boron suboxides, but a very small amount of BH<sub>3</sub> is polymerized to form B<sub>2</sub>H<sub>6</sub>, B<sub>4</sub>H<sub>10</sub>, and other more complex boron hydrides. The scheme for such a polymerization, occurring during the hydrolysis of magnesium boride, was first given by Wiberg [20].

The purpose of the present work was a preliminary examination of the chemistry of processes occurring during the solution of titanium, zirconium, and chromium borides in acids (mainly in hydrochloric acid).

For this purpose, we investigated the resistance of these borides in a powder and sintered form to HCl, H<sub>2</sub>SO<sub>4</sub>, and HNO<sub>3</sub> in comparison with certain acid-resistant compounds (B<sub>4</sub>C and MoSi<sub>2</sub>) and also studied the gaseous hydrolysis products and the composition of the solutions obtained. The data obtained confirmed the above point of view on the chemistry of the decomposition of borides in acids.

#### Chemical Resistance of Titanium, Zirconium, and Chromium Borides in Acids

The boride samples investigated were obtained by three methods: 1) by carbon reduction of a mixture of metal and boron oxides at a temperature of the order of 1900° [21,22]; 2) by the boron carbide method with reduction in vacuum\* [23]; 3) by electrolysis of melts by the method described by Andrieux [24]. The compositions of the starting materials investigated are given in Table 1.

X-ray phase analysis confirmed that all the borides investigated contained well-formed crystal lattices of diborides.

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\* These samples were kindly provided by G. V. Samsonov.



The samples were sintered by hot pressing in graphite molds at 1800° and a pressure of about 100 kg/cm<sup>2</sup> [26]. As a result, we obtained flat disks 25 mm in diameter and 3-4 mm thick. Halves of such disks were used for testing chemical resistance. The samples were placed in beakers with the appropriate acid and left at room temperature for a given time without stirring and then the samples were washed with water and weighed.

In the study of the chemical resistance of powders, the latter were washed after testing on a tared glass filter.

The results of the tests are given in Tables 2 and 3. The data in Table 2 show that electrolytic zirconium and titanium borides also dissolve in acids to a considerable extent, but somewhat less than borides prepared by the boron carbide and carbothermal methods. Table 3 gives comparative data for hot-pressed boron carbide and molybdenum silicide. As follows from the data obtained, these substances have the maximum chemical resistance to acid. Sintered samples of TiB<sub>2</sub> had such a high resistance to hydrochloric acid that they could probably be recommended as acid-resistant materials. Zirconium boride was strongly attacked in hydrochloric acid.

The data in Table 3 show that the addition of metallic silicon to TiB<sub>2</sub> and ZrB<sub>2</sub> reduced the chemical resistance of samples to all the acids tested (HCl, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub>).

#### Hydrolysis Products of Zirconium, Titanium, and Chromium Diborides

In the decomposition of diborides by hydrochloric acid it is possible to establish by smell that appreciable amounts of boron hydrides are formed, especially in the case of zirconium and chromium borides. When treated with hydrochloric acid, chromium boride began to liberate boron hydrides in the cold, while zirconium boride, even in the most crystalline form, for example, that prepared electrolytically, reacted vigorously with hydrochloric acid solution after slight heating, also with the liberation of boron hydrides. The reaction proceeded more slowly with titanium boride and therefore, in order to detect the smell of boron hydrides, it was necessary to use a large sample of boride and carry out the decomposition with heating.

For all three borides, the formation of boron hydrides during the reaction with hydrochloric acid was demonstrated by qualitative reactions with paper moistened with AgNO<sub>3</sub> solution (browning or blackening of the paper) and decolorization of a drop of KMnO<sub>4</sub> solution [27], and also quantitatively by absorption of the gases liberated with water and alkali solution, with subsequent determination of the amount of boric acid in the solution. The latter method was described by Mikheeva [28] and by others [29]. The results of the experiments are given in Table 4.

The detection of boric acid on absorption of the gaseous products with water and alkali solution showed that both diborane and tetraborane were formed during decomposition of the borides. Analysis of the gas collected when the borides were decomposed in a stream of nitrogen showed that after the boron hydrides had been absorbed in water and alkali, the residual gases contained a considerable amount of hydrogen. Thus, it was confirmed that as in the hydrolysis of magnesium and beryllium borides, the gaseous decomposition products consisted of boron hydrides and hydrogen. Quantitative data on the amount of boron hydrides and hydrogen liberated during the decomposition of borides with HCl (1 : 2) are given in Table 5.

TABLE 2

Chemical Resistance of Powdered Zirconium and Titanium Borides Obtained Electrochemically.  
 Boride Powder Fraction <0.2 mm.

Acid	Acid concentration	Experiment conditions	Duration of treatment (in hr)	Degree of solution (in %)	Notes
ZrB <sub>2</sub>					
H <sub>2</sub> SO <sub>4</sub>	1.10	In the cold	0.5	None	Did not react
	Conc.	In the cold	96	3.99	
	1.10	Boiling	1	27	Almost all dissolved solution turbid
	Conc.	Boiling	1		
HNO <sub>3</sub>	1.10	In the cold	0.5	None	Did not react
	1.10	Boiling	1	14	
	Conc.	In the cold	96	74.5	Solution became yellow
		Boiling	1	93.1	Residue became white
HF	1.10	In the cold	24	77	Evolution of gases
	1.10	Boiling	1	86.2	
	Conc.	In the cold	24	84.4	Weak evolution of gases
	1.10	In the cold	16.8	7	
HCl	1.10	Boiling	1	25.7	Violent evolution of gases
	Conc.	In the cold	24	2	
	Conc.	Boiling	1	25.4	Strong evolution of gases
	Water	In the cold	24	5.75	
	Boiling	1	0.94		
TiB <sub>2</sub>					
H <sub>2</sub> SO <sub>4</sub>	1.10	In the cold	168	45.7	
	Conc.	In the cold	96	5.5	
		Boiling	1	43.3	
HNO <sub>3</sub>	1.10	In the cold	96	97.5	Yellow solution
	1.10	Boiling	1	95.5	
	Conc.	In the cold	24	97	
HF	1.10	In the cold	27	15.6	
	Conc.	In the cold	96	16.6	
HCl	1.10	In the cold	96	3.9	Evolution of gases
	1.10	Boiling	1	12	
	Conc.	In the cold	24	5.5	
	Conc.	Boiling	1	12	

TABLE 3

Comparative Data on the Chemical Resistance of Hot-Pressed Boride Sinters to Acids

Composition of samples	Acid and its specific gravity	Weight loss (in % of original sample) after a time of		
		1 day	4 days	10 days
ZrB <sub>2</sub>	HCl, 1.19	2.5	4.9	10.4
	HNO <sub>3</sub> , 1.42	5.6	13.6	33.3
	H <sub>2</sub> SO <sub>4</sub> , 1.84	1.2	4.2	5.2
TiB <sub>2</sub>	HCl, 1.19	0.1	0.4	0.8
	HNO <sub>3</sub> , 1.42	6.1	15.1	30.5
	H <sub>2</sub> SO <sub>4</sub> , 1.84	0.1	0.4	1.0
ZrB <sub>2</sub> +5%Si	HCl, 1.19	0.4	2.0	17.0
	HNO <sub>3</sub> , 1.42	2.5	16.6	53.1
	H <sub>2</sub> SO <sub>4</sub> , 1.84	0.2	1.2	7.8
TiB <sub>2</sub> +5%Si	HCl, 1.19	0.8	2.1	13.3
	HNO <sub>3</sub> , 1.42	3.1	14.2	30.8
	H <sub>2</sub> SO <sub>4</sub> , 1.84	0.04	0.7	1.4
TiB <sub>2</sub> +10%Si	HCl, 1.19	0.1	0.5	1.1
	HNO <sub>3</sub> , 1.42	6.33	48.77	Disintegrated
	H <sub>2</sub> SO <sub>4</sub> , 1.84	3.85	5.2	34.29
TiB <sub>2</sub> +20%Si	HCl, 1.19	0.04	0.18	0.25
	HNO <sub>3</sub> , 1.42	4.43	9.69	19.8
	H <sub>2</sub> SO <sub>4</sub> , 1.84	0.80	2.82	34.2
B <sub>4</sub> C	HCl, 1.19	0.24	0.59	0.65
	HNO <sub>3</sub> , 1.42	0.41	0.65	0.65
	H <sub>2</sub> SO <sub>4</sub> , 1.84	1.05	1.05	1.53
B <sub>4</sub> C+10%Si	HCl, 1.19	0.07	0.10	0.10
MoSi <sub>2</sub>	HCl, 1.19	0.09	0.16	0.74
	HNO <sub>3</sub> , 1.42	0.46	0.94	1.56
	H <sub>2</sub> SO <sub>4</sub> , 1.84	0.07	0.01	0.07

TABLE 4

Demonstration of the Formation of Boron Hydrides During Hydrolytic Decomposition of Borides in Hydrochloric Acid (1 : 1)\*

Composition of boride and experimental conditions	Sample (in g)	Result of qualitative reaction for boron hydrides			B content detected by absorption (in % of sample)	
		organo-leptically	reaction with AgNO <sub>3</sub>	reaction with KMnO <sub>4</sub>	in water	in KOH solution
ZrB <sub>2</sub> with heating	0.1	+	Brown spot	None		
The same	1.0	++	Black spot	Decolorization	0.1 - 1	0.3 - 0.4
The same in the cold	5.0	+++	Black spot	Decolorization		
TiB <sub>3</sub> in the cold	5.0	None	None	None		
The same with heating	5	++	Black spot	Decolorization	0.6 - 0.7	0.4 - 0.5
CrB <sub>3</sub> in the cold	5	Traces	None	None		
The same with heating	5	+++	Black spot	Decolorization	0.2 - 0.3	0.06 - 0.08

\* The decomposition was carried out in a stream of purified argon.

TABLE 5

Amounts of Boron Hydrides and Hydrogen Liberated During the Decomposition of ZrB<sub>2</sub>, TiB<sub>3</sub>, and CrB<sub>3</sub> in Boiling Hydrochloric Acid (1 : 2)

Boride	Method of preparing boride	Total boron content of boron hydrides relative to sample (in %)	Number of moles of H <sub>2</sub> per mole of boride	Boride	Method of Preparing boride	Total boron content of boron hydrides relative to sample (in %)	Number of moles of H <sub>2</sub> per mole of boride
ZrB <sub>2</sub>	Electrochemical	1.86	3.95	TiB <sub>3</sub>	Boron carbide	1.52	0.48
		1.12	3.95			1.13	0.40
		1.27	4.00			1.02	0.504
		0.90	4.07			0.27	3.65
		0.60*	4.10			0.16	3.73
ZrB <sub>2</sub>	Boron carbide	1.34	4.10	CrB <sub>3</sub>	Boron carbide	0.42	3.50

\* HCl concentration 1 : 4.

Analysis of the insoluble residues remaining after decomposition of the borides with hydrochloric acid and of the solution obtained showed the ratio of boron to metal in the residue and solution to be practically unchanged, as can be seen from the data in Table 6. The slight deviations found (especially for  $\text{CrB}_2$ ) are probable explained by analysis \* errors due to the presence of solid hydrolysis products in the residue and also a trace of the boride  $\text{Cr}_3\text{B}_4$  (Table 7).

It should be noted that, judging by the color of the solutions formed during solution of the borides and also by qualitative tests applied to them, the solution of  $\text{ZrB}_2$  yielded  $\text{ZrOCl}_2$  solution,  $\text{TiB}_2$  gave  $\text{TiCl}_3$  solution, and  $\text{CrB}_2$  gave  $\text{CrCl}_3$  solution.

Table 8 gives data on the relative rate of decomposition of powdered zirconium, titanium, and chromium borides when they were boiled with hydrochloric acid. As follows from these data, the rate of decomposition depended to a large extent on the degree of crystallinity of the boride (preparation method).

As the data obtained show, chromium boride dissolved most rapidly and titanium boride, least rapidly, which is in accordance with previously presented data on the loss in weight of boride sinters and powders.

#### Chemistry of the Decomposition of Borides in Acids

The data obtained naturally are insufficient for a complete explanation of the chemical processes occurring during solution of borides in hydrochloric acid. However, the fact that boron hydrides and hydrogen are liberated simultaneously during hydrolysis indicates that they are connected. If we write the over-all equations for hydrolysis of borides, considering that it goes to boric acid, we get for borides of tetravalent metals:  $\text{MeB}_2 + 7\text{H}_2\text{O} \rightarrow \text{Me(OH)}_4 + \text{B}_2\text{O}_3 + 5\text{H}_2$  (1); for trivalent metals:  $\text{MeB}_2 + 6\text{H}_2\text{O} \rightarrow \text{Me(OH)}_3 + \text{B}_2\text{O}_3 + 4.5\text{H}_2$  (2); for divalent metals:  $\text{MeB}_2 + 5\text{H}_2\text{O} \rightarrow \text{Me(OH)}_2 + \text{B}_2\text{O}_3 + 4\text{H}_2$  (3).

If boron suboxides are formed during the hydrolysis, even partially, the amount of hydrogen liberated must be correspondingly smaller. Thus, if it is assumed that  $\text{B}_2\text{O}_3$  is formed as the suboxide, as was proposed, for example by Ray for the hydrolysis of magnesium borides [31], instead of the first equation we would have:  $\text{MeB}_2 + 6\text{H}_2\text{O} \rightarrow \text{Me(OH)}_4 + 2\text{BO} + 4\text{H}_2$  (4), and instead of equation (3):  $\text{MeB}_2 + 5\text{H}_2\text{O} \rightarrow \text{Me(OH)}_3 + 2\text{BO} + 3.5\text{H}_2$  (5). As 4 moles of hydrogen was liberated during the hydrolysis of zirconium diboride and a salt of tetravalent zirconium was formed in the solution, it may be assumed that the hydrolysis of  $\text{ZrB}_2$  proceeds according to equation (4). In the hydrolysis of  $\text{CrB}_2$ ,  $\text{Cr}^{+++}$  ions and 3.5 to 3.7 moles of  $\text{H}_2$  were obtained, i.e., the reaction proceeded according to equation (5).

Only in the case of titanium boride was the amount of hydrogen much less than that corresponding to any of the schemes presented. The reason for this is not clear. The equations presented are only over-all. The formation of both  $\text{B}_2\text{H}_6$  and  $\text{B}_4\text{H}_{10}$  during hydrolysis shows that in all probability the hydrolysis of transition metal borides also proceeds through the formation of the primary boron hydride radical  $\text{BH}_2$ . Depending on the rates of its formation, hydrolytic decomposition, the polymerization, the degree of which may also depend on catalytic factors, the amount of boron hydrides which may be collected is different for different borides and also depends on the hydrolysis

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\*The borides were analyzed by Blumenthal's method.[30].

conditions. Thus, for example, it was minimal for  $\text{CrB}_2$  and almost 5 times greater for  $\text{ZrB}_2$  and  $\text{TiB}_2$ . The factors determining the course of these reactions have not been studied sufficiently yet and due to this it is impossible to write a developed scheme for the hydrolysis of the borides investigated, considering the formation of primary boron hydrides.

TABLE 6

Chemical Analysis of Original Borides and Solutions Obtained After Decomposition in Hydrochloric Acid

Boride	Analysis of original boride (in%)		Sample (in g)	Weight of residue (in g)	Analysis of residue (in %)		Analysis of solution (in %)	
	Me	B			Me	B	Me	B
$\text{ZrB}_2$	80.0	18.2	0.512	0.242	79.5	18.5	73.0	17.8
	80.0	18.2	0.357	0.099	--	18.2	69.0	18.6
	78.6	19.9	0.200	0.002	--	--	--	19.0
$\text{TiB}_2$	68.4	29.6	2.154	2.052	68.5	30.2	--	21.3
	68.4	29.6	2.072	1.942	--	30.8	--	23.2
$\text{CrB}_2$	69.8	26.9	2.015	0.205	75.1	23.2	--	25.8
	69.8	26.9	2.307	0.197	--	23.4	--	25.8

TABLE 7

X-ray Diffraction Analysis of Original Borides and Residues Obtained After Decomposition in Hydrochloric Acid

Boride	X-ray analysis of original material	X-ray analysis of insoluble residue
$\text{ZrB}_2$	Pure $\text{ZrB}_2$ phase	$\text{ZrB}_2$ + oxide compounds
$\text{TiB}_2$	Pure $\text{TiB}_2$ phase	$\text{TiB}_2$
$\text{CrB}_2$	$\text{CrB}_2$ + trace of $\text{Cr}_2\text{B}_4$	$\text{Cr}_2\text{B}_4$

TABLE 8

Data on the Rate of Decomposition of Boride Powders in Boiling HCl (1:2). Experiments Carried out with 50 ml of HCl

Boride	Sample (in g)	Duration of experiment (in hr)	Amount of boride dissolved (in g)	Rate of solution (in g/ hr per g of sample)
ZrB <sub>2</sub> "electrolytic"	0.383	2	0.267	0.347
	0.512	1.5	0.270	0.352
	0.357	2.5	0.258	0.290
	0.426	1.25	0.238	0.446
	1.663	4	1.160	0.175
ZrB <sub>2</sub> "boron carbide"	2.033	0.5	1.610	1.580
	2.053	0.5	1.632	1.590
TiB <sub>2</sub> "boron carbide"	2.154	0.5	0.101	0.094
	2.073	0.5	0.130	0.120
CrB <sub>2</sub> "boron carbide"	2.015	0.5	1.809	1.79
	2.307	0.5	2.110	1.82

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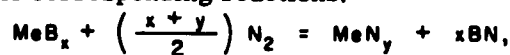
SELECTED ARTICLE NO 4  
PHYSICAL CHEMISTRY  
HEATS OF FORMATION OF BORIDES OF SOME TRANSITION METALS (Ref: 34)

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(Translation by S.A. Mersol)

In view of the increasing requirements for borides of transition metals, the determination of the heats of formation of corresponding boride phases becomes particularly important. Partial facts on this subject have been published recently, in which during an analysis of the tensimetric curve of the formation of  $TiB_2$ , the heat of formation of  $TiB_3$  was determined by the vacuum-thermal method, and was found to be equal to  $\sim 70.04$  kcal/mole (1).

In Brewer's and Haraldsen's work (2) the thermodynamic stability of borides of refractory metals, Ti, Zr, Nb, Ta, Cr, Mo, and W (also Ce and Th), were discussed. To determine the approximate values of the heats of formation of the borides, they used the data on the stability of borides to nitrogen and carbon; these data were obtained by X-ray analysis of the products of corresponding reactions:



In such an analysis if no solubility of the initial components or of the reaction products takes place, or if no other new compounds are formed, it is possible to determine the approximate values of heats of formation of borides, as well as those of boron nitrides and carbides from values established by previous investigations (see data in table 1).

TABLE 1 (2)  
THE HEATS OF FORMATION OF BORIDES OF TRANSITION METALS

BORIDE	$\Delta Q$ KCAL/MOLE	BORIDE	$\Delta Q$ KCAL/MOLE	BORIDE	$\Delta Q$ KCAL/MOLE	BORIDE	$\Delta Q$ KCAL/MOLE
$TiB_2$	$\sim 72$	$NbB_2$	$> 36$	$MoB$	16.3	$W_2B_5$	25 - 45
$Ti_2B_8$	$> 105$	$TaB_2$	$> 52$	$MoB_2$	23.0	$CeB_4$	$< 84$
$ZrB$	$> 39$	$CrB_2$	$> 30$	$Mo_2B_8$	50.0	$ThB_4$	$> 52$
$ZrB_2$	$> 78$	$Mo_2B$	25.5	$W_2B$	20 - 28	$ThB_6$	$> 66$
$ZrB_{12}$	$> 120$	$Mo_3B_2$	42.0	$WB$	12 - 22	—	—

Note that the general thermodynamic stability of the compounds which transition metals form with metalloids like boron, carbon, and nitrogen is, in large degree, determined not only by the reaction kinetics of the compounds being formed, but also by the degree of matching of the electronic configuration and the atom of the metal (or non-metal) whereby energetically the least stable is more directly affected. Matching the electronic configuration to the atom of the metal or nonmetal must be accompanied by the formation of energetically more stable states, in which either the d-orbitals of metal

atoms are "filled up" or there is a release of energy close to the ionization energy of the nonmetal atom (3). It follows, then that the smallest heats of formation values of the molecules are found in carbides (ionization potential of carbon  $I_c = 11.22$  eV), and much greater values in nitrides ( $I_n = 14.47$  eV), borides ( $I_b = 8.4$  eV) and silicides ( $I_{si} = 7.39$  eV)\*. As to the filling up of d-orbitals of transition metal atoms having various electronic defects, it seems proper to assume that within each transition period the heats of formation must decrease with a corresponding decrease in electronic defect of the metal.

In Table 2 values are listed for the heats of formation of borides, carbides, and nitrides of transition metals per mole of the phase and per g-atom of the nonmetal.

TABLE 2  
HEATS OF FORMATION OF BORIDES, CARBIDES, AND NITRIDES

METAL	HEAT OF FORMATION IN KCAL								
	BORIDE			CARBIDE			NITRIDE		
	PHASE	PER MOLE OF PHASE	PER G ATOM OF B	PHASE	PER MOLE OF PHASE	PER G ATOM OF C	PHASE	PER MOLE OF PHASE	PER G ATOM OF N
Ti	TiB <sub>2</sub>	72	36	TiC	57.25	57.25	TiN	80.3	80.3
V	VB <sub>2</sub>	—	—	VC	28.0	28.0	VN	60.0	60.0
Cr	CrB <sub>2</sub>	>30	>15	Cr <sub>3</sub> C <sub>2</sub>	21.01	10.50	CrN	29.5	29.5
Zr	ZrB <sub>2</sub>	>78	>39	ZrC	44.1	44.1	ZrN	82.2	82.2
Nb	NbB <sub>2</sub>	>36	>18	NbC	19.0	19.0	NbN	59.0	59.0
Mo	MoB <sub>2</sub>	23	11.5	MoC	-4.2	-4.2	MoN	17.0	17.0
Hf	HfB <sub>2</sub>	—	—	HfC	—	—	HfN	—	—
Ta	TaB <sub>2</sub>	>52	>26	TaC	38.5	38.5	TaN	58	58
W	W <sub>2</sub> B <sub>5</sub>	25 — 45	5 — 9	WC	-8.4	-8.4	WN	17	17

Additionally, the determination of the heats of formation is largely dependent on the nonmetal's ionization potential. By increasing the number of metalloid atoms per metal atom (as in boride phases) the heat of formation of the bond Me-B (Q per 1 boron atom) decreases as a result of the transition its electrons make to form covalent bonds B-B. More specifically (from the data in table 1), it follows that

$1/2 \text{ TiB}_2 \sim 36$	$\text{Mo}_2\text{B} \quad 25.5$
$1/2 \text{ Ti}_2\text{B}_5 > 21$	$1/2 \text{ Mo}_3\text{B}_2 \quad 21$
$\text{ZrB} > 39$	$\text{MoB} \quad 16.3$
$1/2 \text{ ZrB}_2 > 39$	$1/2 \text{ MoB}_2 \quad 11.5$
$1/2 \text{ ZrB}_{12} > 10$	$1/5 \text{ Mo}_2\text{B}_8 \quad 10.0$

There is an increase in the tendency toward the formation of individual structural elements from boron atoms in the borides of transition metals (4). In figure 1 the data of table 2 on the heats of formation of boride, carbide, and nitride phases per one g-atom of the metalloid are shown graphically. For nitride and carbide phases within each transition period the Q values plot as straight lines, which enables us to extrapolate the heats

\* Without the calculation of the metalloid-metalloid bonds.

of formation of HfC and HfN (not heretofore mentioned in the literature). These values are ~ 81 and ~ 97 kcal/mole, respectively. In diborides the boron atoms form horizontal lattices, perpendicular to the axis z, with layers of boron and metal atoms alternating in the arrangement ANAN. Changes in the positioning of the atoms in the horizontal lattices in  $\text{Mo}_2\text{B}_5$  and  $\text{W}_2\text{B}_5$  result in a relatively abrupt increase in the heat of formation for the Me-B bond, which, in turn, upsets the straight-lined dependency. However, this upset is taking place also in the boride phases  $\text{CrB}_2$  and  $\text{MoB}_2$ , with structures like  $\text{AlB}_2$ , as well as in the rest of the borides. This reaction is apparently associated with those properties of the chromium and molybdenum atomic structure to which L. Pauling (5) first directed attention, i.e., that chromium contains only 5.78 bond electrons and is characteristically close to the elements of the iron triad and to the platinoids. This situation causes a relatively slow weakening of the electronic configuration to take place and in the observed phenomenon of unusually high values for the heats of formation of boron bonds. As the graphs in figure 1 indicate, it is impossible to determine the heats of formation of borides and other phases of iron, cobalt, and nickel by means of simple extrapolation.

An analogous picture (figure 2) is also obtained by the expression of heats of formation depending on the oxidizability (3) of transition metal atoms using

$$\epsilon = \frac{1}{N_n},$$

where n equals the number of electrons and N equals the principal quantum number of vacant d-orbital spaces. This shows the presence of a deep bond between the heats of formation and the state of the electronic configuration of carbides, nitrides, and borides.

By the method described in reference 1 we also determined the heats of formation of diborides of zirconium (63.1 kcal/mole) and chromium (19.0 kcal/mole)\*. We calculated the  $\Delta Q$  of borides according to Kubashevskiy (6) by making use of the change in the molar volume at the formation of the compounds from the elements. Besides this, the data on the heats of formation of borides were obtained by extrapolation using the rectilinearity of the change  $\Delta Q$  with the change of the metal atomic number in analogous phases, starting with the tensimetric value  $\Delta Q_{\text{TiB}_2} = 70.04$  kcal/mole. All these data are listed in table 3.

TABLE 3  
THE COMPARISON OF THE HEATS OF FORMATION  
OF BORIDES ACCORDING TO VARIOUS DATA

BORIDE	HEAT OF FORMATION IN KCAL			
	BY DATA FROM (2)	BY DATA FROM TENSIMETRIC EXPERIMENTS	CALCULATION ACCORDING TO (6)	EXTRAPOLATION BY GRAPHS OF FIGS. 1 AND 2
$\text{TiB}_2$	~ 72	70.04	73	—
$\text{ZrB}_2$	> 78	63.1	65	60
$\text{VB}_2$	—	—	62	24
$\text{NbB}_2$	> 36	—	59	33.5
$\text{TaB}_2$	> 52	—	63	45.0
$\text{CrB}_2$	> 30	19.0	47	—
$\text{MoB}_2$	22.5	—	60	—
$\text{W}_2\text{B}_5$	25 — 45	—	49	—

\* The data on the chromium boride were obtained jointly with R.B. Kotelnikov.

It is possible to calculate from the established data the approximate values for the heats of formation of diborides of Ti, Zr, Nb, Ta, and Cr whereby the calculation by extrapolation apparently gives better results than those obtained by Kubashevskiy's empirical formula.

#### SUMMARY

A comparison was made between the numerical values of the heats of formation of borides of several transition metals of groups IV, V, and VI in the periodic system. These values were obtained through calculations and were determined as a result of tensimetric experiments and the study of the products of the interaction of borides with nitrogen and carbon. It was shown that the heats of formation of compounds similar to metals (borides, carbides, and nitrides of transition metals) are determined by the distribution of the electron configuration in their crystal lattices.

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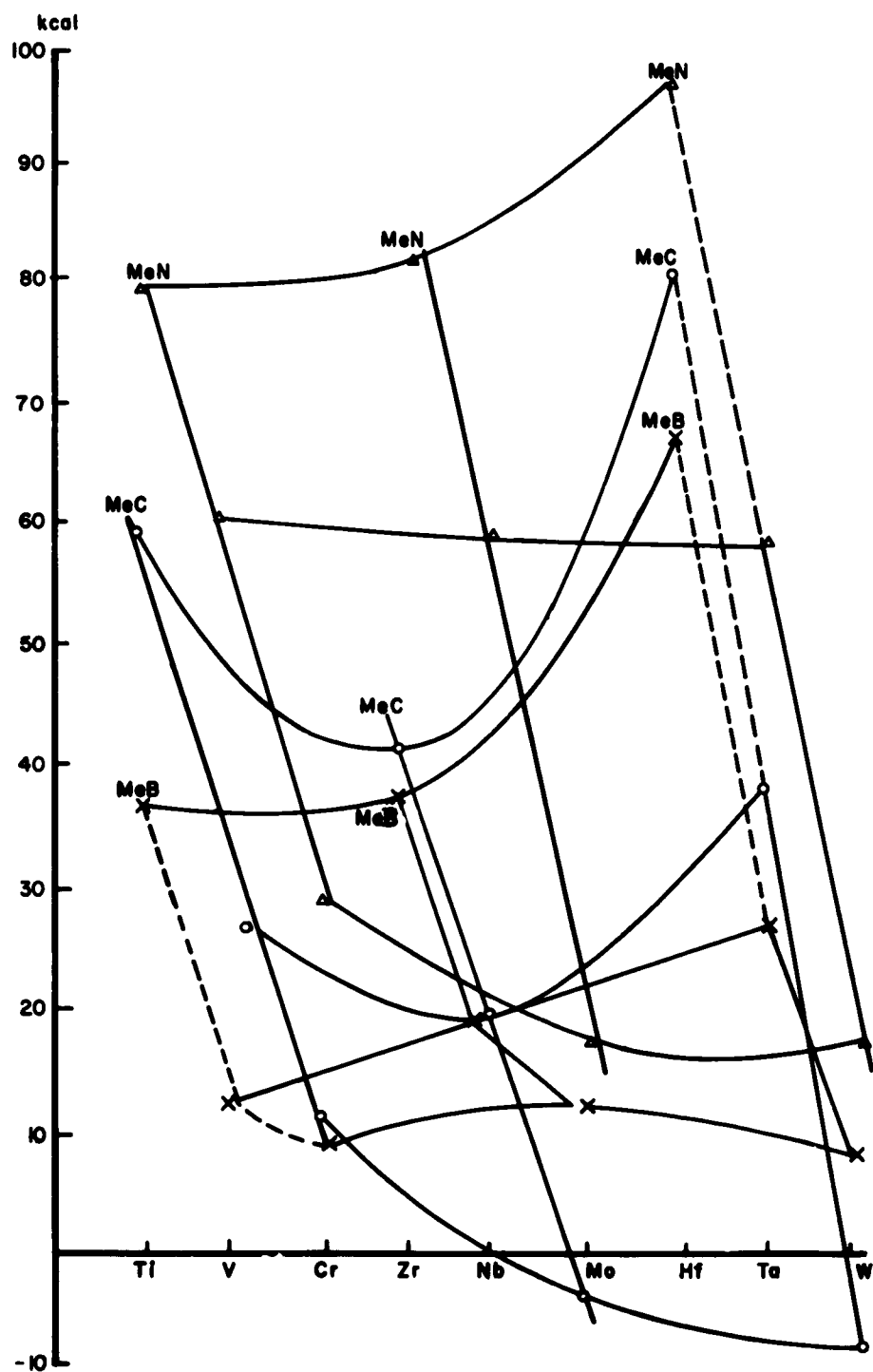


Figure 1. The heats of formation of carbides, borides, and nitrides (per 1 g-atom of metalloids).

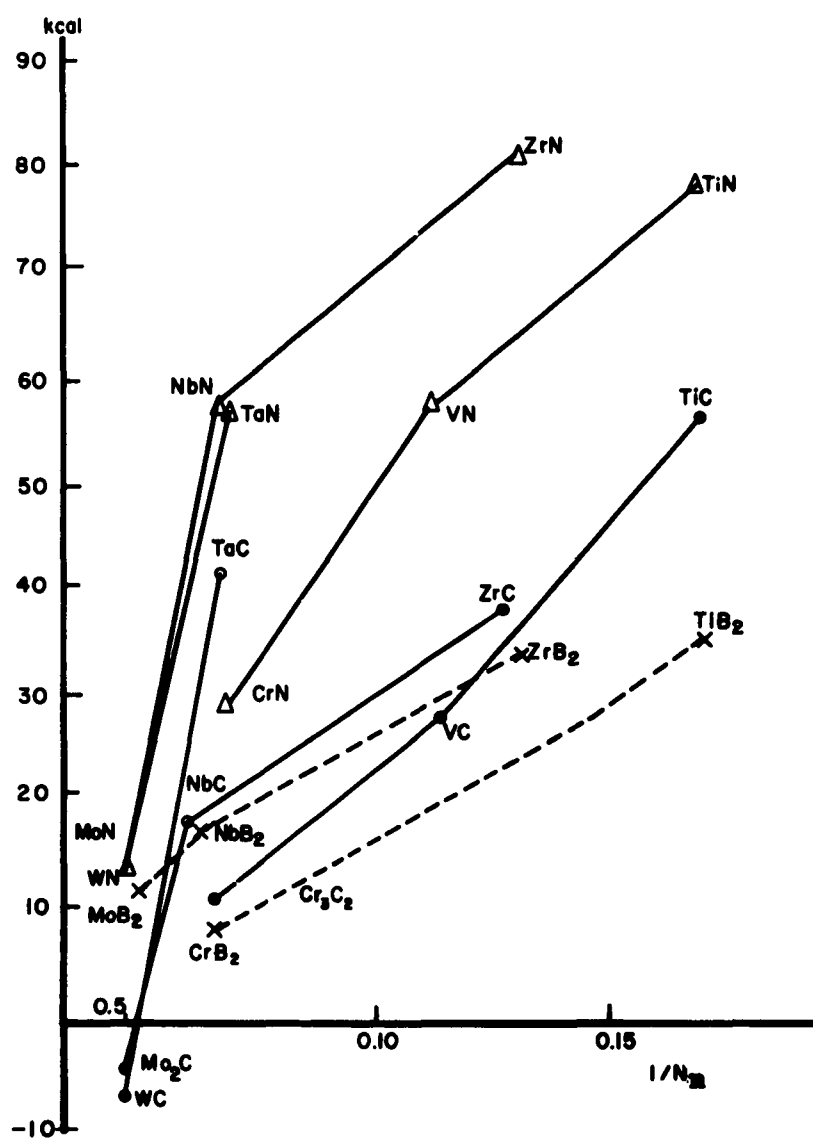


Figure 2. The relationships between the heats of formation of carbides, borides, and nitrides, and the value  $1/N_n$  for transition metals.

Aeronautical Systems Division, Dir/Materials and Processes, Applications Lab, Wright-Patterson AFB, Ohio.  
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Unclassified Report

A comprehensive review of the literature was made to assist in providing background information needed for future work concerning boride materials. The materials reviewed included solid bodies of TiB<sub>2</sub>, ZrB<sub>2</sub>, HfB<sub>2</sub>, VB<sub>2</sub>,

( over )

NbB<sub>2</sub>, TaB<sub>2</sub>, CrB<sub>2</sub>, and ThB<sub>4</sub>. This compilation presents information on synthesis, properties, and applications of the selected boride compounds, including selected abstracts and articles.

This documentary search, by showing many gaps and wide scatter where information is available, demonstrates the need for the development of authoritative scientific information on borides applicable to future technological requirements.

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